Advances in Our Understanding of the Major Sources Contributing to Ambient Particulate Matter in California

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ARB Chair's Seminar Series
January 22, 2008

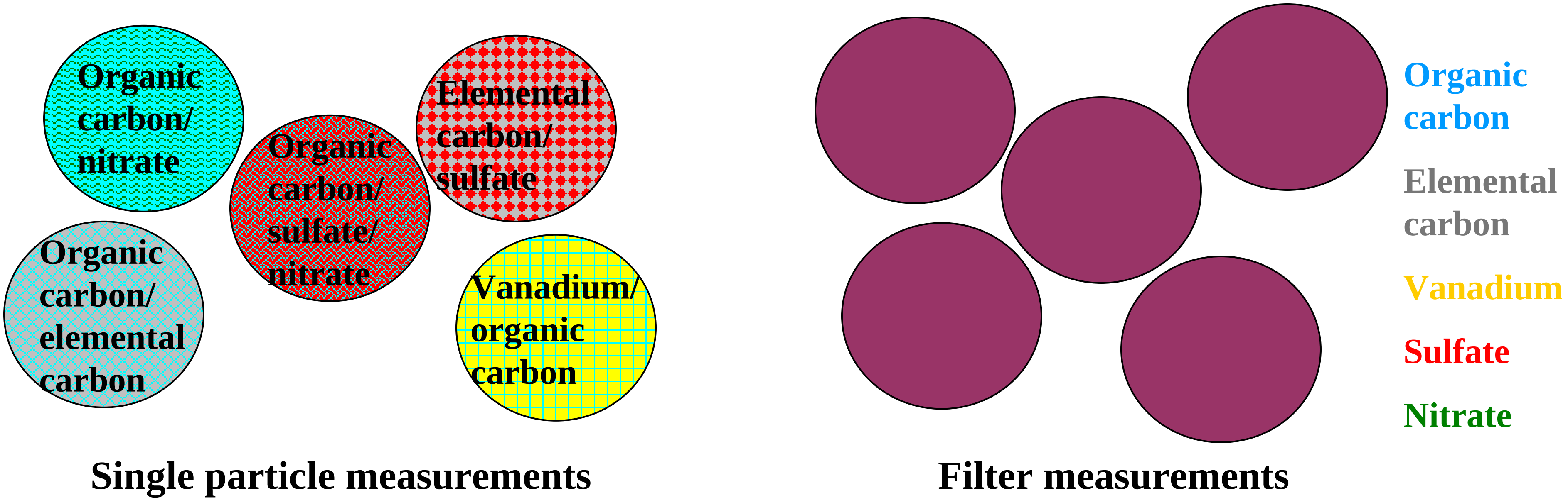
Overview

- On-line single particle analysis using ATOFMS
  - Aerodynamic size, chemistry, and optical properties of individual particles
  - Measures single particle chemistry of dust, soot, OC, sea salt, biomass, metals
  - Up to 50,000 particles per hour
- California studies -- San Diego, Riverside, Los Angeles, Long Beach, Fullerton, Fresno, Angiola, Mexican/US border region
- The road to ambient source apportionment using ATOFMS
  - Establish source signature libraries for single particles
  - Use for ambient source apportionment of PM
  - Will focus on San Diego Freeway Study
  - Challenges in apportioning aged particles (1° vs. 2 °)
- Ongoing ATOFMS studies

Understanding Aerosol Mixing State

Aerosol mixing state impacts:

- Absorption/scattering properties (radiative forcing)
- Cloud condensation nuclei activity
- Identification of sources
- Evaluation of health risks

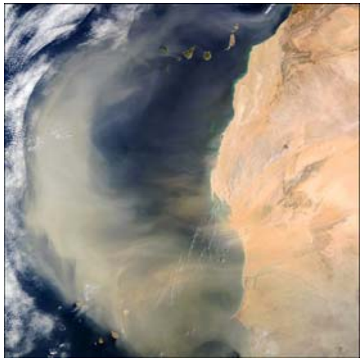


Sources of Atmospheric Aerosols

Gasoline Vehicles

Industry

Volcanoes



Dust

Diesel Vehicles

Ships

Biomass Burning

Sea Salt

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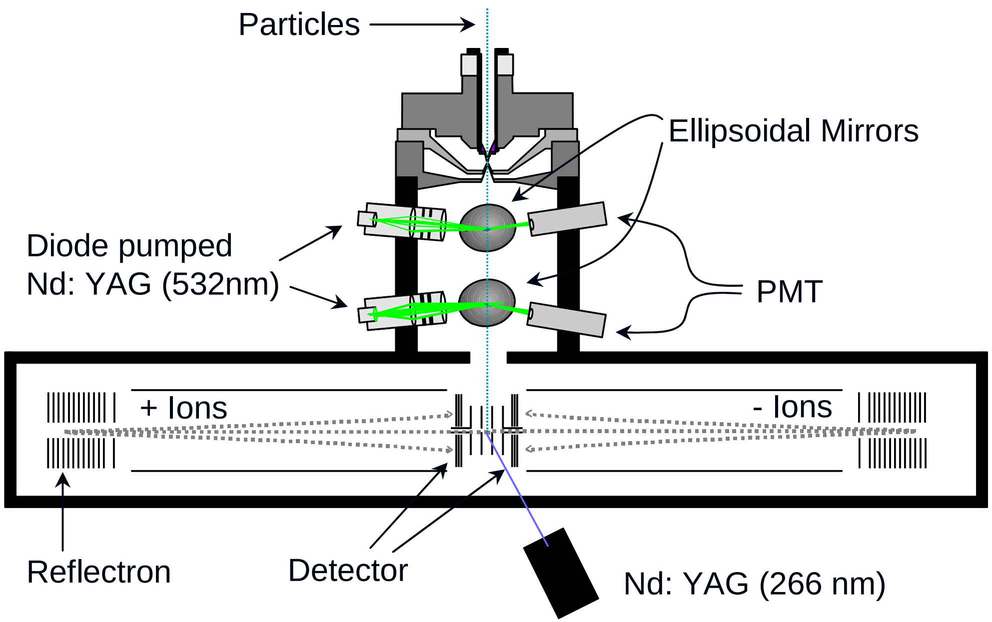
Images from www: nasa.gov; old-picture.com; mit.edu; esa.int; ewh.ieee.org; whitehouse.gov; andaman.org

Aerosol Time-of-Flight Mass Spectrometry



Standard inlet ATOFMS

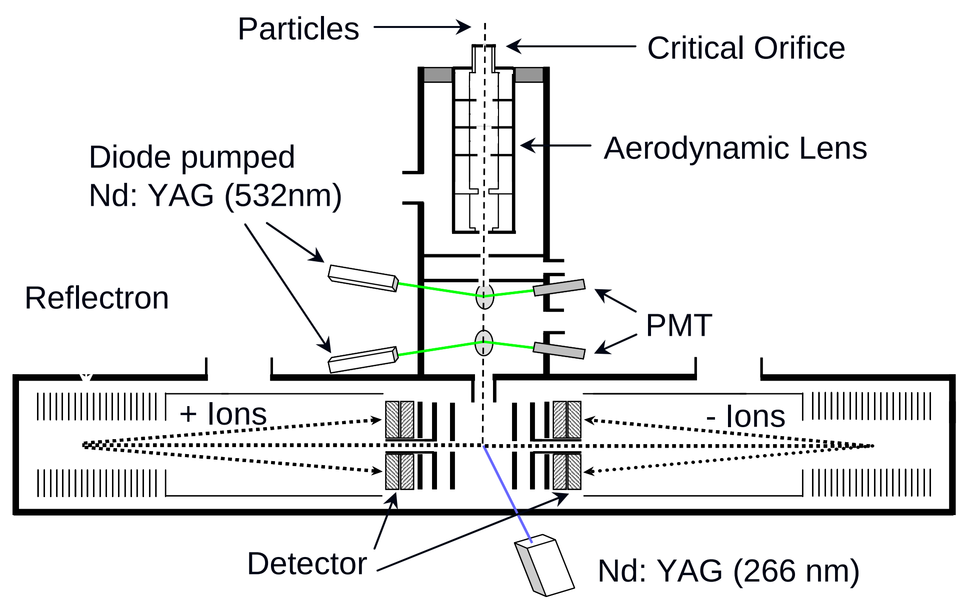
(200 – 3000 nm)

Gard, E., J.E. Mayer, B.D. Morrical, T. Dienes, D.P. Fergenson, and K.A. Prather, *Analytical Chemistry*, *69* (20), 4083-4091, 1997.

UF–ATOFMS

(50 – 300 nm)

Su, Y., M.F. Sipin, H. Furutani, and K.A. Prather, *Analytical Chemistry*, *76* (3), 712-719, 2004.



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Creating Source Signatures (Seeds)

1) Dynamometer and source tests
   - Cars, trucks, biomass burning, meat cooking, coal, biofuels

2) Ambient seeds
   - Roadside sampling
   - Use short time bursts

Vehicle Signature Library

Goal: Establish an ATOFMS source signature library that can distinguish between similar sources. We began with two very chemically similar PM sources.

HDDV 2001
Standard inlet ATOFMS

7 HDDVs tested ranging from 1985 - 2000

Shields, L.G., D.T. Suess, and K.A. Prather, *Atmospheric Environment*, *41* (18), 3841-3852, 2007.

LDV 2002
UF-ATOFMS
Standard inlet ATOFMS

28 LDVs tested ranging from 1953 - 2003

Sodeman, D.A., S.M. Toner, and K.A. Prather, *Environmental Science & Technology*, *39* (12), 4569-4580, 2005.

HDDV 2003
UF-ATOFMS
Standard inlet ATOFMS

6 HDDVs tested ranging from 1985 - 2000

Toner, S.M., D.A. Sodeman, and K.A. Prather, *Environmental Science & Technology*, *40* (12), 3912-3921, 2006.

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List of Cars and Cycles

Table S1: List of make: model: year: and mileage for each vehicle: as well as the technology category: cycles tested and total particles analyzed by UF-ATOFMS (50 – 180nm) and ATOFMS (300 – 2550nm)

#	Make	Model	Year	Mileage	Category	Cycles	UF-ATOFMS	ATOFMS
1	Toyota	Camry	1999	43160	LEV	1C	225	56
2	Nissan	Sentra	1999	52630	LEV	1C	425	120
3	Honda	Civic	1996	77703	LEV	1C	729	105
4	Chevrolet	Monte Carlo	2002	20230	LEV	1C	262	195
5	Honda	Accord	1998	97811	LEV	1C	381	248
6	Ford	Explorer	1998	82513	LEV	1C	319	90
7	Nissan	Pathfinder	2002	8169	LEV	1C	484	338
8	Chevrolet	Silverado	2003	1264	LEV	1C	721	275
9	Jeep	Grand Cherokee	2000	31751	LEV	1C	746	93
10	Toyota	Tacoma	2000	51554	LEV	1C	345	247
11	Plymouth	Horizon	1988	32097	TWC	1C:2C	165:154	158:253
12	Toyota	Camry	1991	95532	TWC	1C:2C	108:143	115:122
13	Acura	Integra	1994	104441	TWC	1C:2C	91:100	53:55
14	Ford	Mustang	1998	10697	TWC	1C:2C	80:74	43:22
15	Ford	Taurus	1991	136983	TWC	1C:2C	212:195	280:281
16	Cadillac	Sedan DeVille	1999	35320	TWC	1C:2C	250:131	258:208
17	Dodge	Caravan	1989	207104	TWC	3H:4H:5H	55:203:83	469:936:188
18	Nissan	Frontier Pickup	1996	55940	TWC	3H:4H:5H	70:154:88	278:987:37
19	Toyota	SR5 Pickup	1989	59231	TWC	3H:4H:5H	159:226:78	259:96:20
20	Suzuki	Samari	1987	57124	TWC	3H:4H:5H	123:181:95	382:1784:52
21	Chevrolet	Suburban	1995	91618	TWC	3H:4H:5H	106:83:53	666:66:78
22	Mercedes	280E	1977	118119	Oxy	1C	118	119
23	Honda	Accord	1980	88642	Oxy	1C	***	397
24	Toyota	Corolla	1979	8661	Oxy	1C	112	131
25	Chevrolet	Bel Air	1953	96176	Non	1C	154	85
26	Ford	Mustang	1966	55280	Non	1C	83	208
27	Chevrolet	S10 Blazer	1993	162750	Smoker	1C	***	69
28	Mercury	Cougar	1968	63622	Smoker	1C	***	1297

LEV = Low Emission Vehicle
TWC = Three Way Catalytic Converter
Oxy = Oxidation Catalytic Converter
Non = No Catalytic Converter
Smoker = exhibits smoke in exhaust

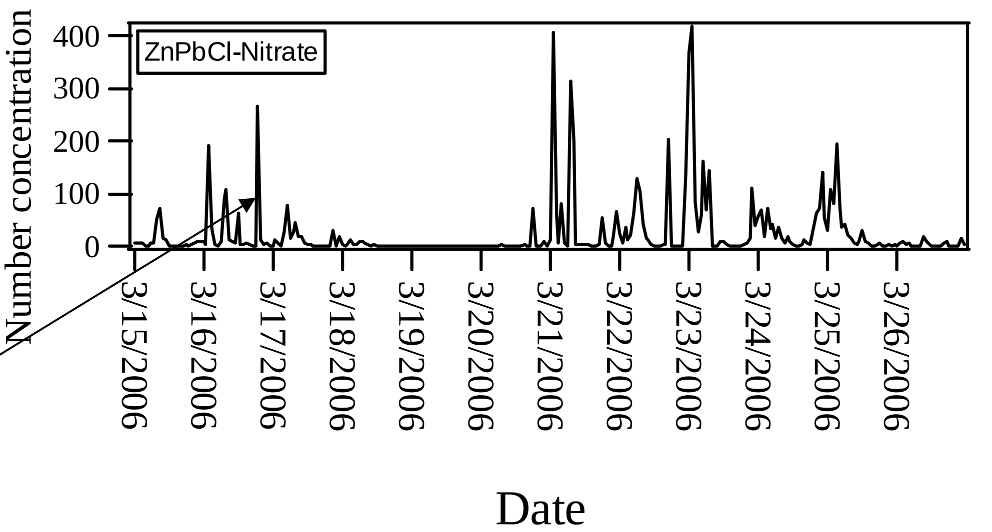
1 = FTP
2 = UC
3 = UC bag 1&2
4 = CC
5 = FTP bag 1&2

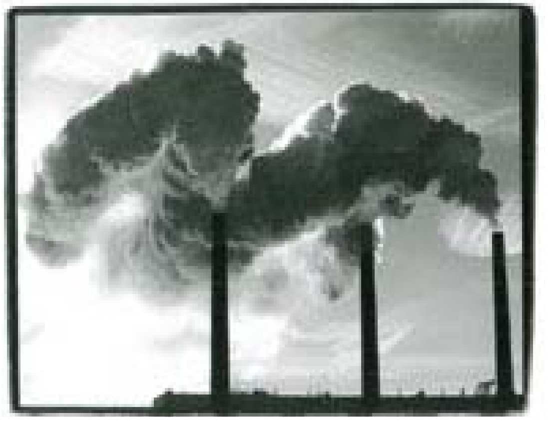
C = Cold Start
H = Hot Start

***: Instrumental issue. See text for explanation

Creating Source Seeds

- Dynamometer and source tests
  - Cars, trucks, biomass burning, meat cooking, coal, biofuels
- Ambient seeds
  - Roadside sampling
  - Use short time bursts
- Create library of source + ambient seeds
- ~150 seeds being used for "on the fly" source apportionment





ATOFMS Source Seeds

- Cars (idle, cruise, accelerate, different years of cars, engine technologies, etc.)
- Trucks (idle, cruise, accelerate, etc.)
- Coal combustion (high, low temps,…)
- Biomass burning I, II, etc.
- Biofuel combustion (agricultural burns, brush fires)
- Ships
- Cooking, charbroiling
- Dust I, II, III, etc.
- Sea salt
- Industrial emissions I, II, III, etc.
- Aged versions of each (created from ambient studies)

Steps in source apportionment

1) Make clusters or “seeds” of major particle types produced by different sources using ART-2a (or another mass spectral clustering tool)

2) Analyze single ambient particles size, chemistry, and optical properties (up to 864,000 particles in one day)

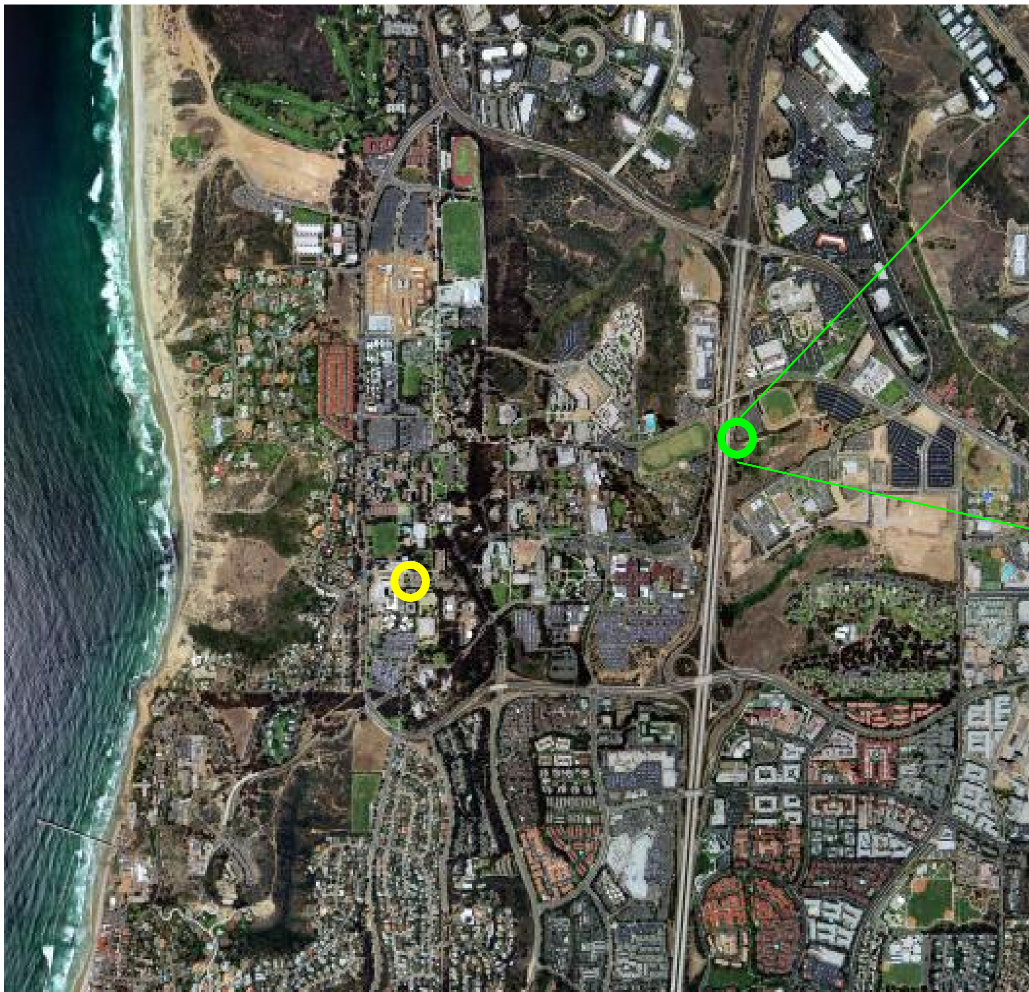
3) Match individual particles against “seeds” from libraries for source apportionment

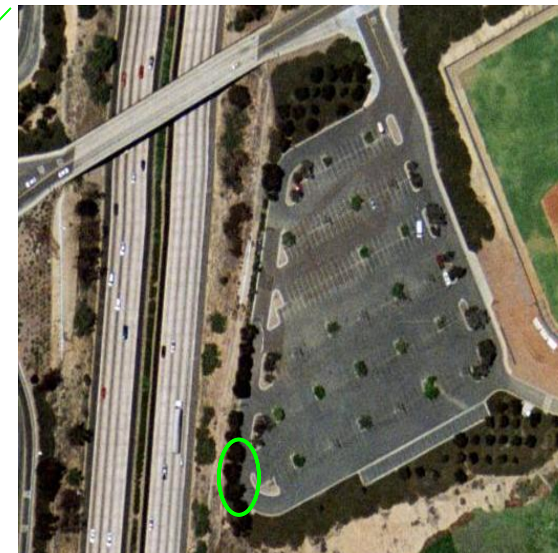
4) Determine size-resolved PM source fractions in real-time (on-the-fly source apportionment)

Freeway Study--Location

- Sampled in an ambient location with fresh vehicle emissions with little aging or influence from other sources
- Location should make an ideal test of dyno source library

http://maps.google.com





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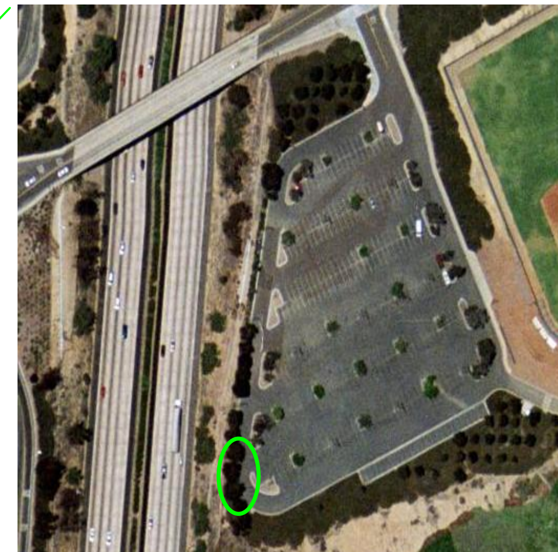
Freeway Study--Conditions

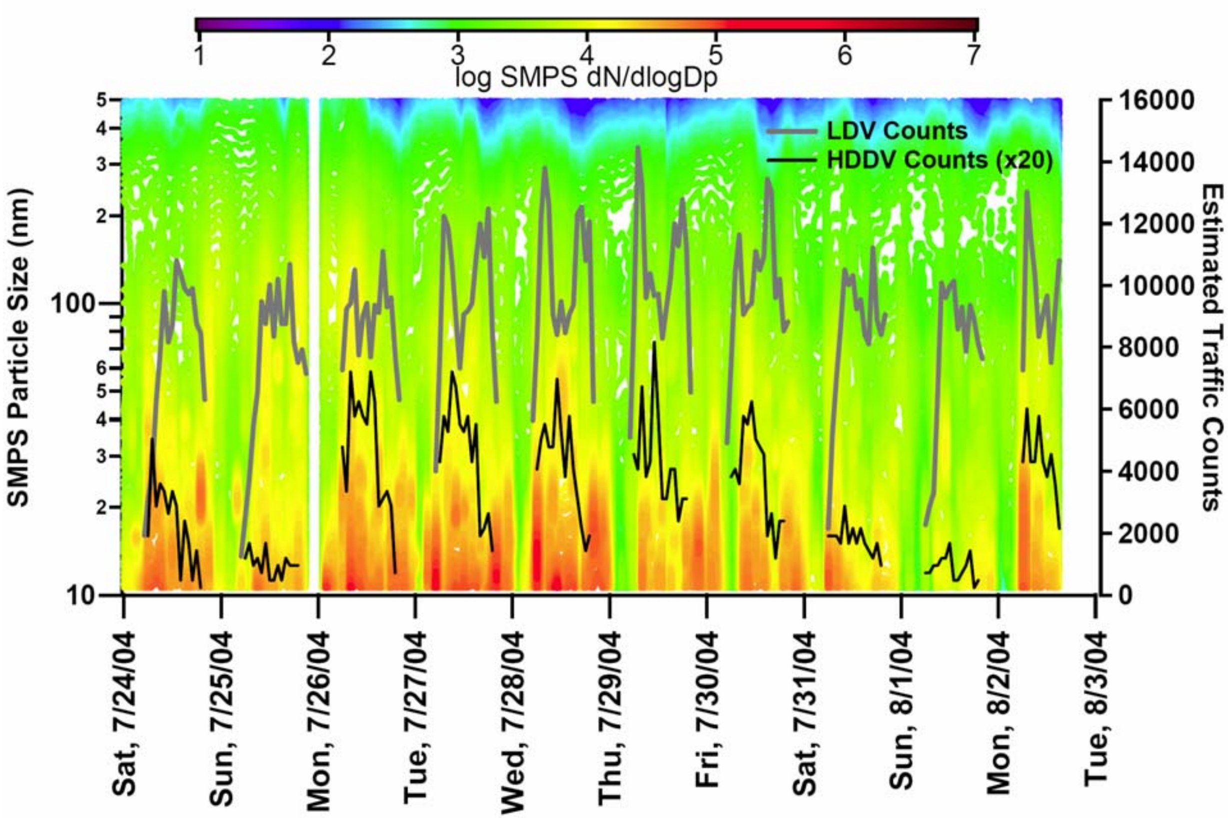
- Conducted from July 21 – August 25, 2004
- Low campus activity and very low traffic in sampling site parking lot
- Daytime winds predominantly blow from west to east

http://maps.google.com



UF Particle Concentration & Traffic

- UF particle concentrations correlate with traffic counts
- Expected, since UF particles come from fresh emission sources



Concentrations & traffic decrease on weekends

HDDV counts decrease more on the weekends than do LDV (particle concentrations may be most influenced by HDDV)

Significant regional background (green)

Scanning Mobility Particle Sizer (SMPS) data along with traffic counts (from video).
HDDV counts are multiplied by 20 to keep them on the same scale as LDV traffic counts.

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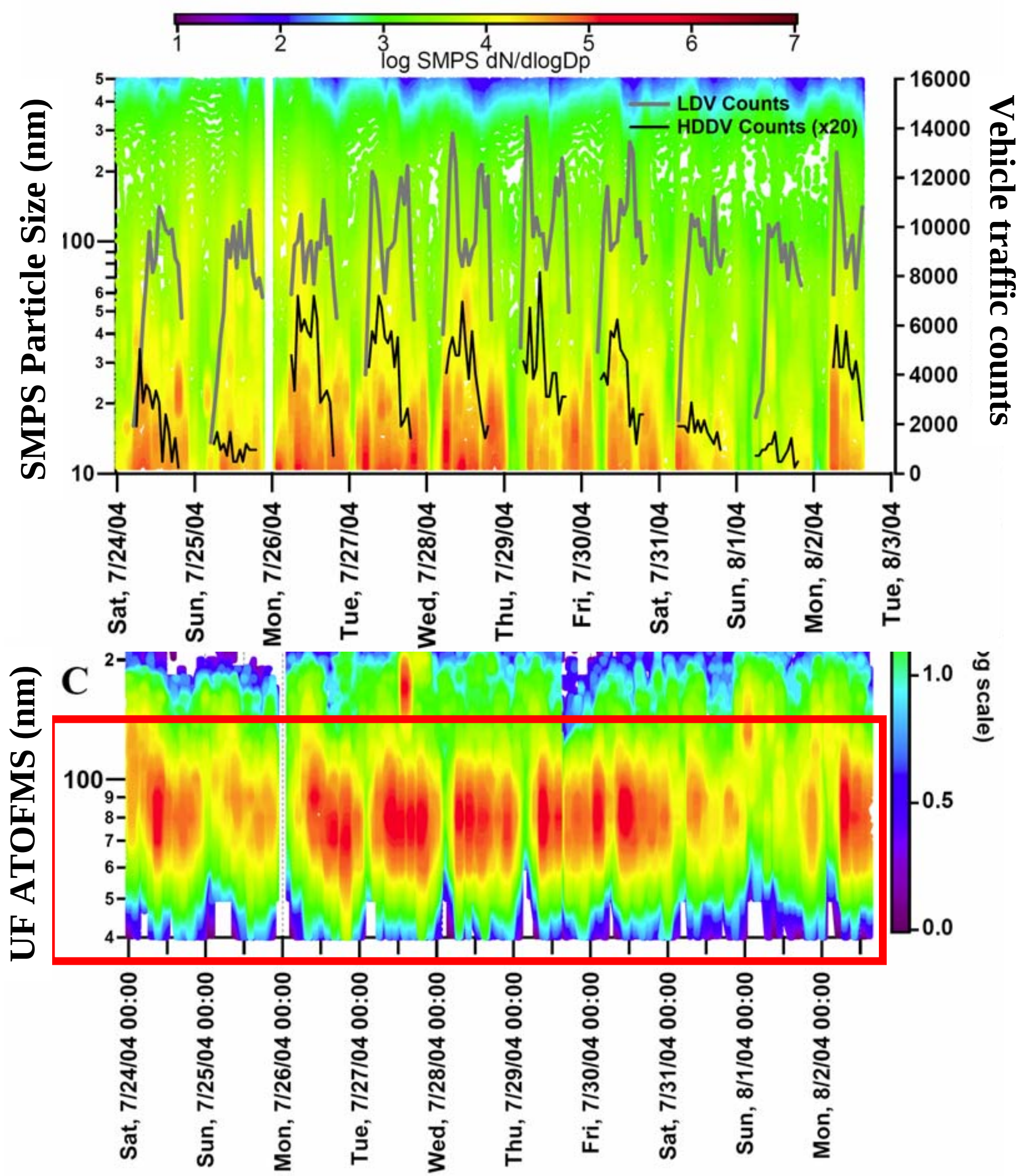
Toner, S.M., L.G. Shields, D.A. Sodeman, and K.A. Prather, *Atmospheric Environment*, *doi:10.1016/j.atmosenv.2007.08.005*, 2007.

Freeway Vehicle Emissions

Freeway particles primarily detected primarily with the UF-ATOFMS

Track vehicle counts
Track UF (SMPS) concentrations



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Toner, S.M., L.G. Shields, and K.A. Prather, Source apportionment of freeway-side $PM_{2.5}$ using ATOFMS, *Atmospheric Environment*, submitted, 2007.

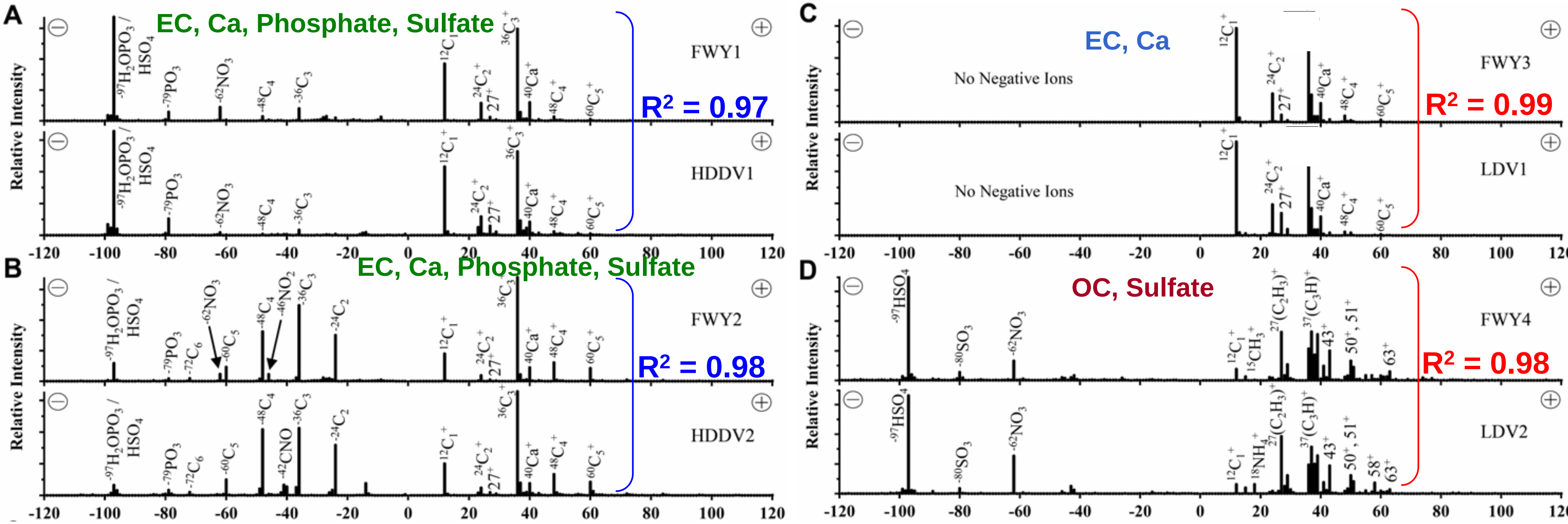
Question #1

Do the top ultrafine (UF) particle types detected near a freeway resemble the dynamometer particle “seeds”?

Top Ultrafine Freeway Types vs. Dyno Types

HDDV Types

LDV Types



- High m/z to m/z R^2 values
- Dynamometer particles are chemically representative of those detected in a fresh emission ambient environment

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Toner, S.M., L.G. Shields, D.A. Sodeman, and K.A. Prather, *Atmospheric Environment, doi:10.1016/j.atmosenv.2007.08.005*, 2007.

Other Questions

- Are there unique set of signatures for the majority of gasoline vs. diesel vehicles?
- For a unique set of clusters, can we match a significant percentage of UF particles?
- What is the split between cars vs. trucks?

Ultrafine particle (50 – 100 nm) apportionment

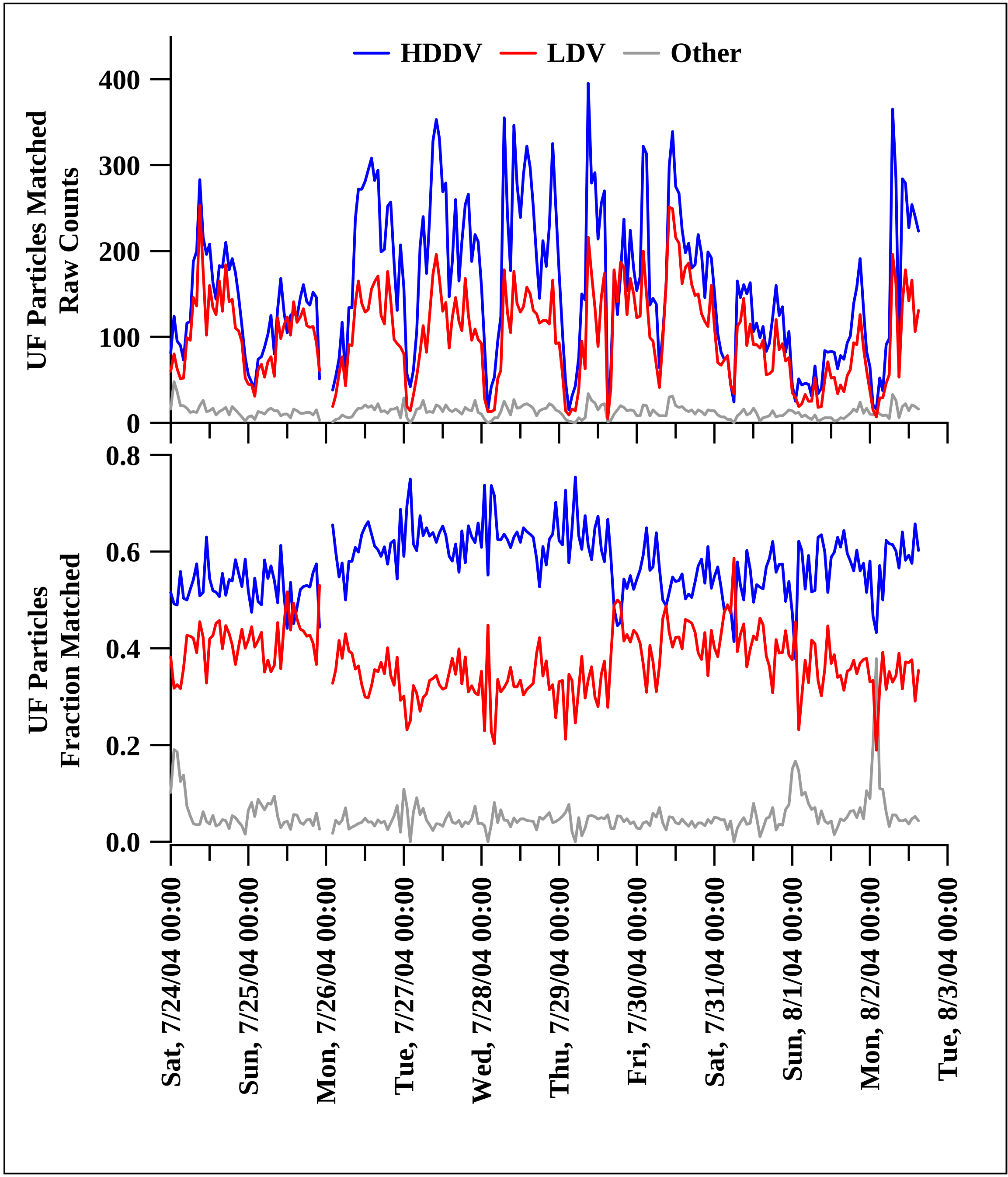
Cars vs. trucks

95% of UF apportioned to vehicles
(58% HDDV & 37% LDV)

UF apportionment tracks traffic counts

HDDV emissions dominate despite relatively low traffic contributions

Weekday vs. weekend differences



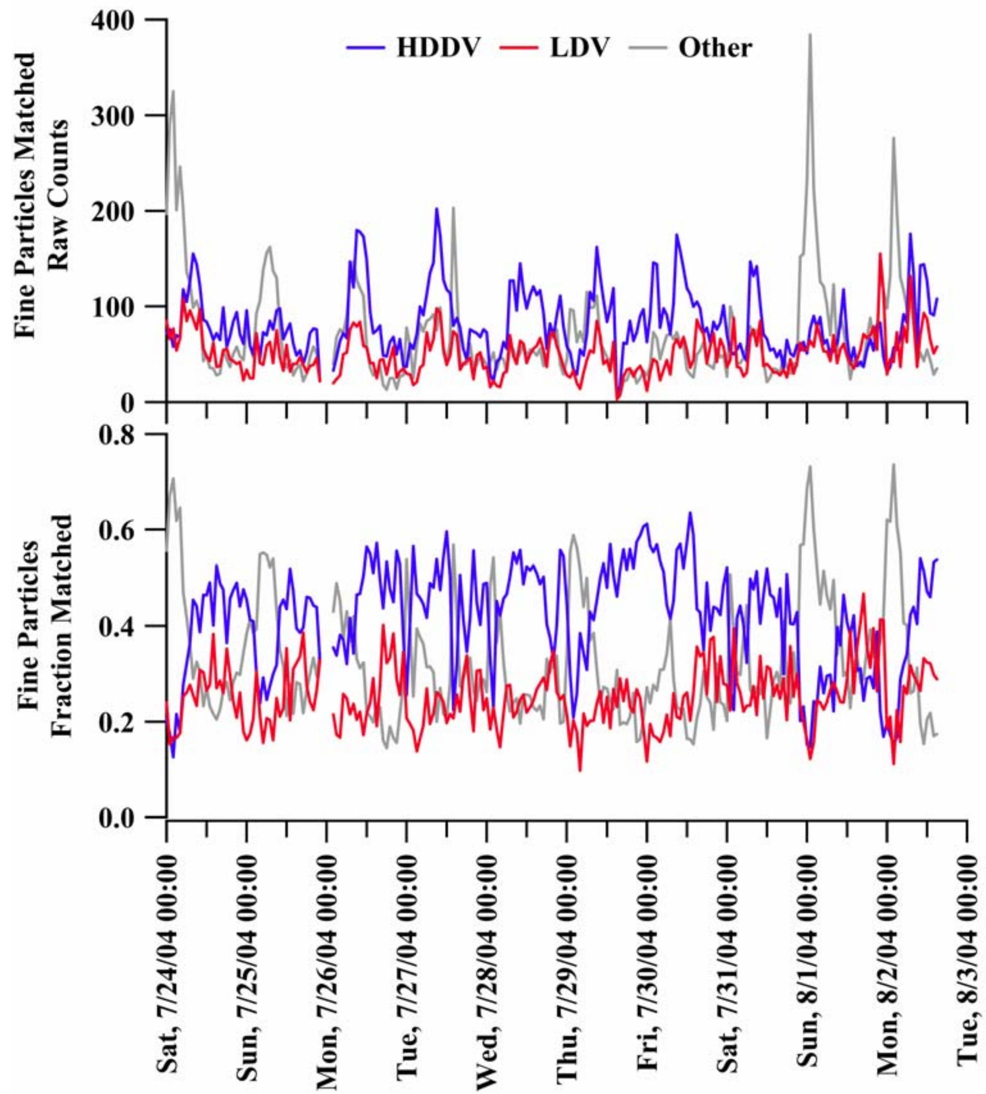
Matching the UF-ATOFMS Freeway Particles to the Vehicle Source Library

Accumulation mode (100 – 300 nm) apportionment

66% of fine mode particles (100 – 300 nm) apportioned to vehicles (41% HDDV & 25% LDV)

HDDV emissions dominate over LDV in the accumulation mode as well.

Shows a larger influence from non-vehicle (other) particles



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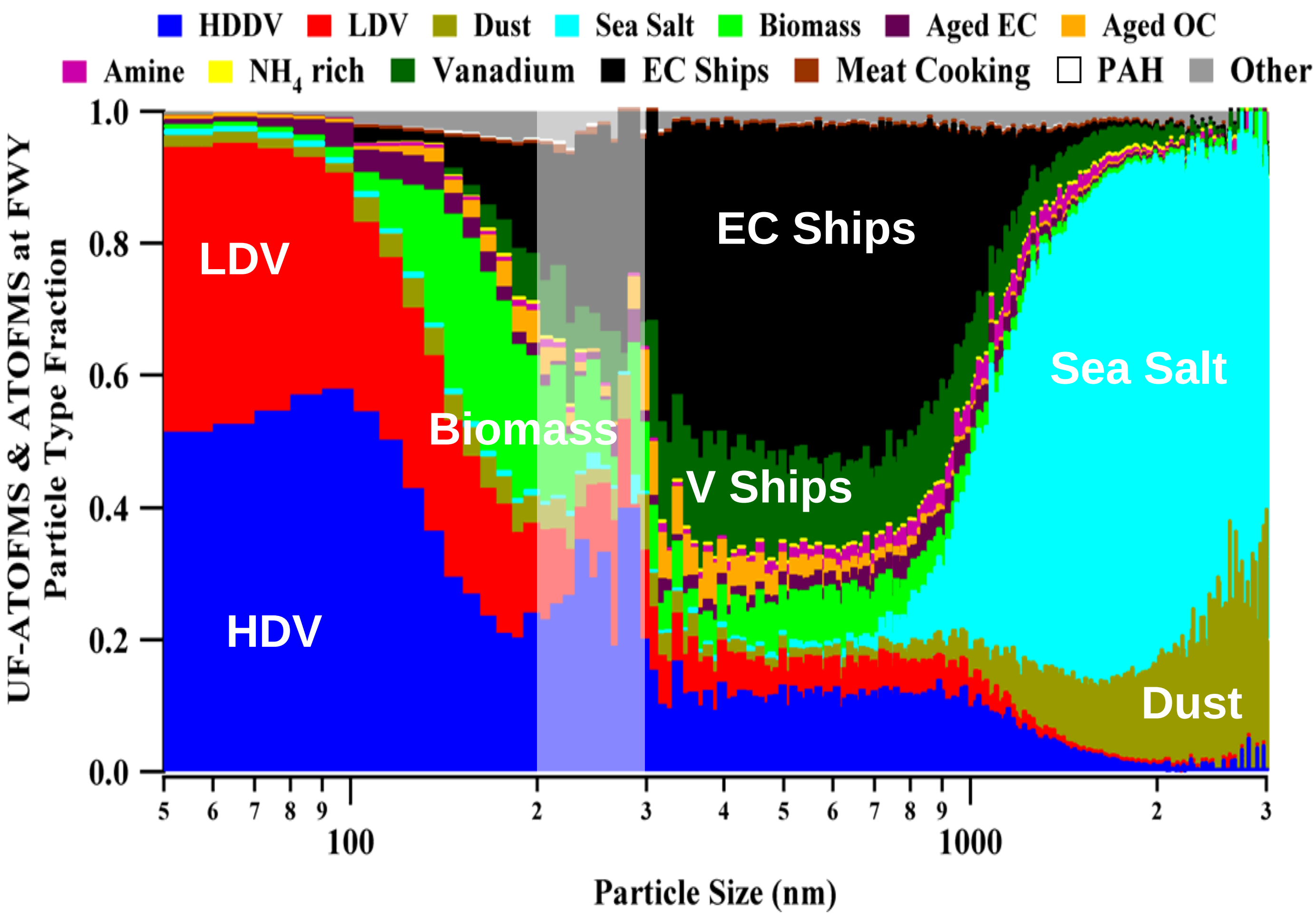
Size-resolved Source Apportionment



50 nm → 3 µm

More aged (secondary components)

Adding More Signatures to the Source Library

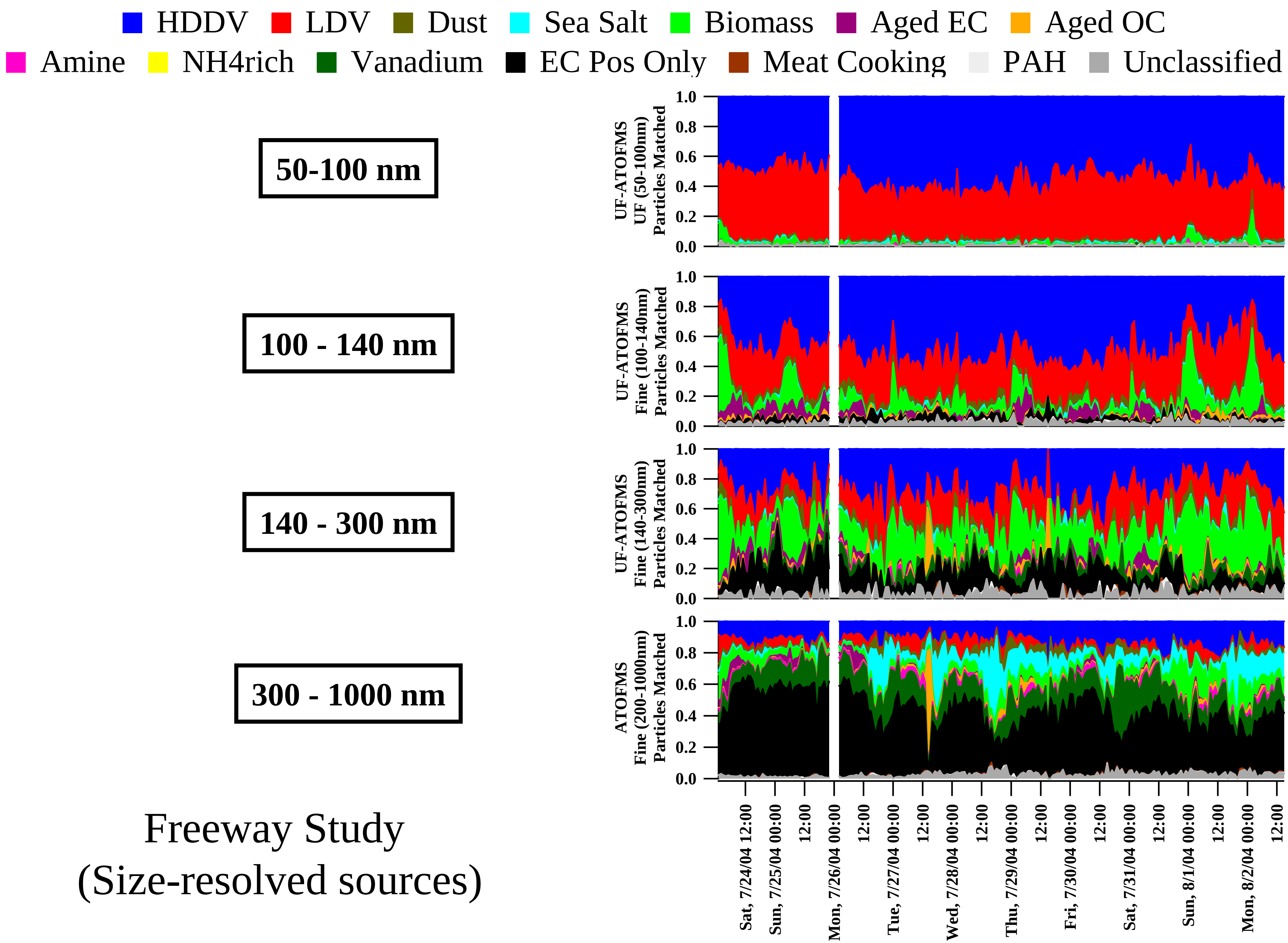
Add more signatures to the library to see if multiple sources can be distinguished without interfering with the HDDV/LDV apportionment

Source signatures from lab and ambient characterization studies were added to the library

- Additional **HDDV** and **LDV** signatures from the freeway study
- **Biomass** burning signatures from lab and ambient characterization studies
- **Dust** signatures from lab and ambient characterization studies
- **Sea salt** from ambient characterization studies
- **Meat cooking** from ambient characterization studies

Additional signatures for non-source specific particle types (from ambient studies)

- **Aged elemental carbon (EC)** and **Aged organic carbon (OC)**
- **Amine-**containing particles
- **Vanadium-**containing particles
- **EC** (from the background type detected during the freeway study)
- **Ammonium-rich** particles
- **PAH-containing** particles



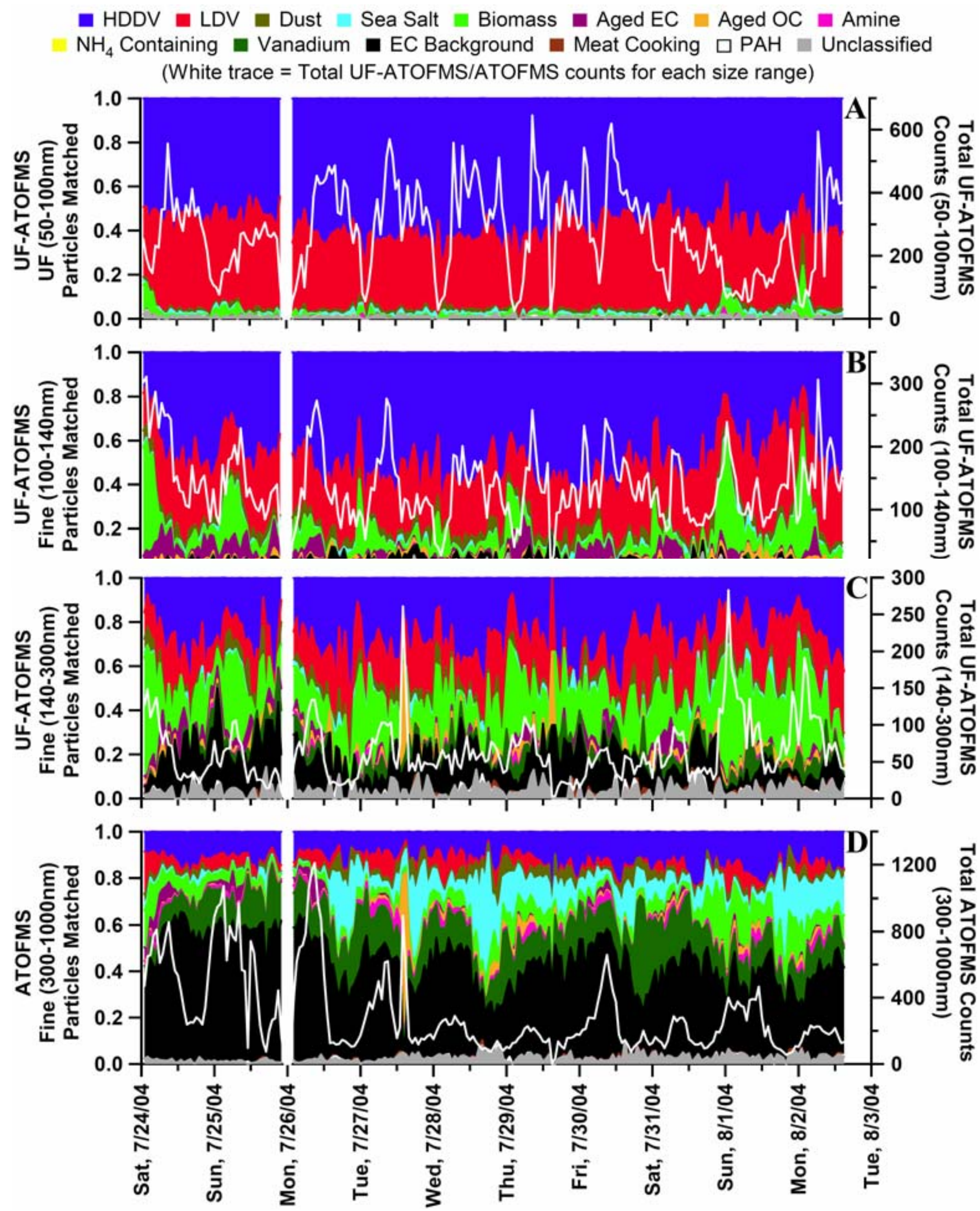
Freeway Study
(Size-resolved sources)

Freeway Particles Matched to Expanded Library

Other (non-vehicle) types begin to dominate with increasing size

Source signature matching technique can distinguish between sources

Regional contributions outweigh vehicle exhaust contributions even near freeway at times



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Toner, S.M., L.G. Shields, and K.A. Prather, Source apportionment of freeway-side $PM_{2.5}$ using ATOFMS, *Atmospheric Environment*, submitted, 2007.

Freeway Background Particle Types

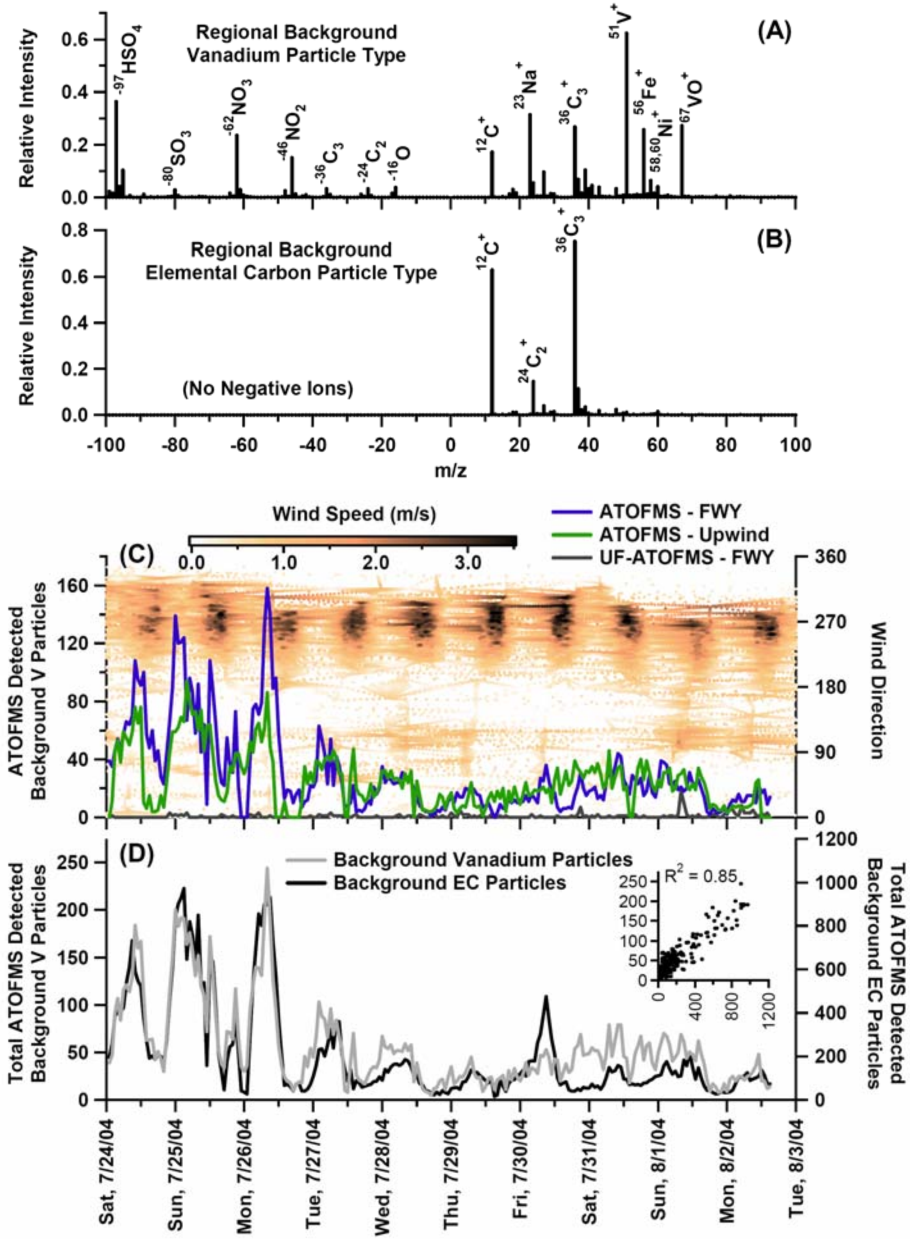
Two main types dominated submicron (300-1000 nm) background particles

- Elemental Carbon
- Vanadium w/ Fe and Ni

The “background” concentrations spike at night – early morning when the wind speeds were lowest

Detected with the standard inlet ATOFMS instruments (0.5-1 μm)

Largest spikes occurred on the first three days of study (7/24 – 7/26)



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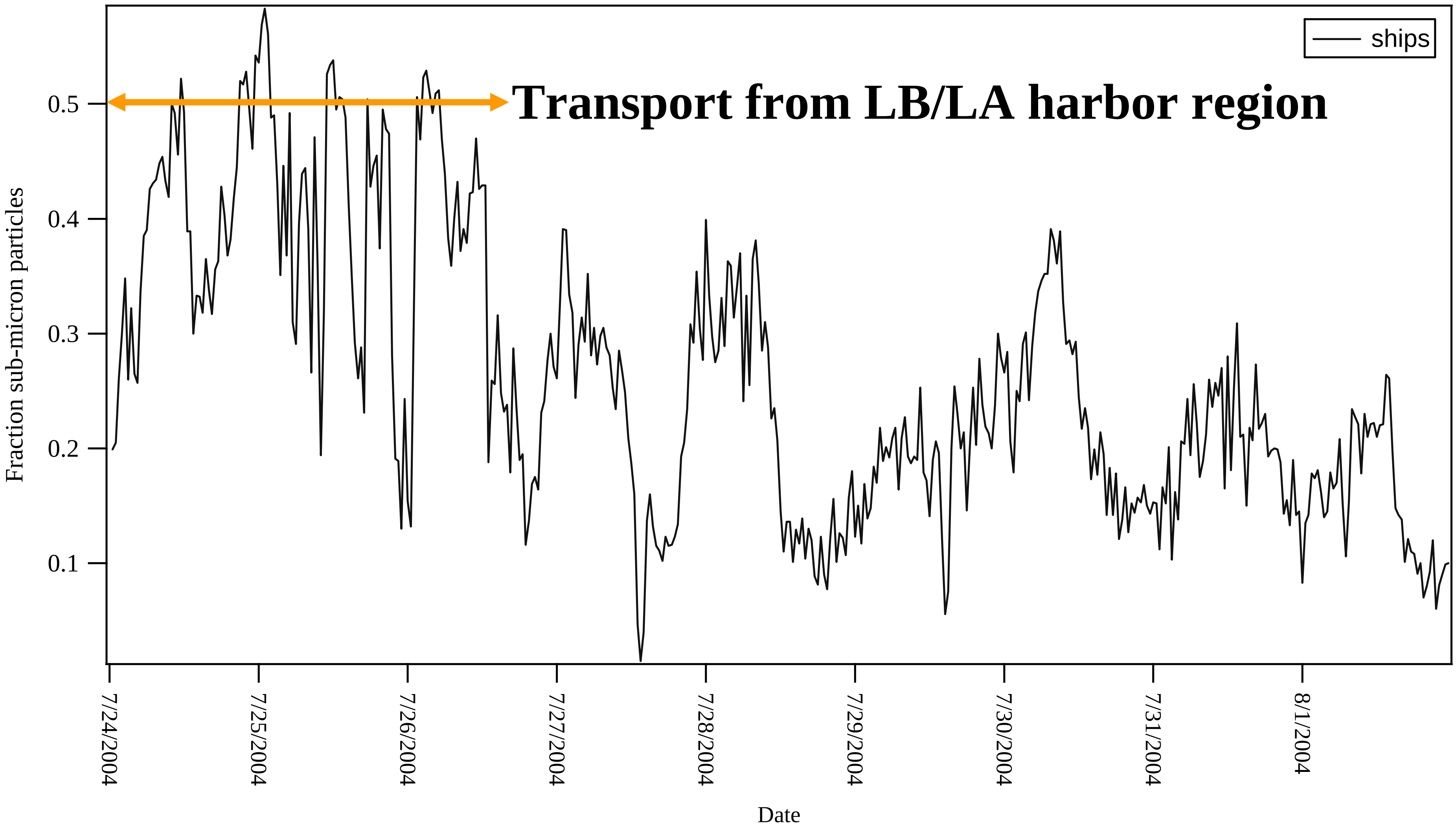
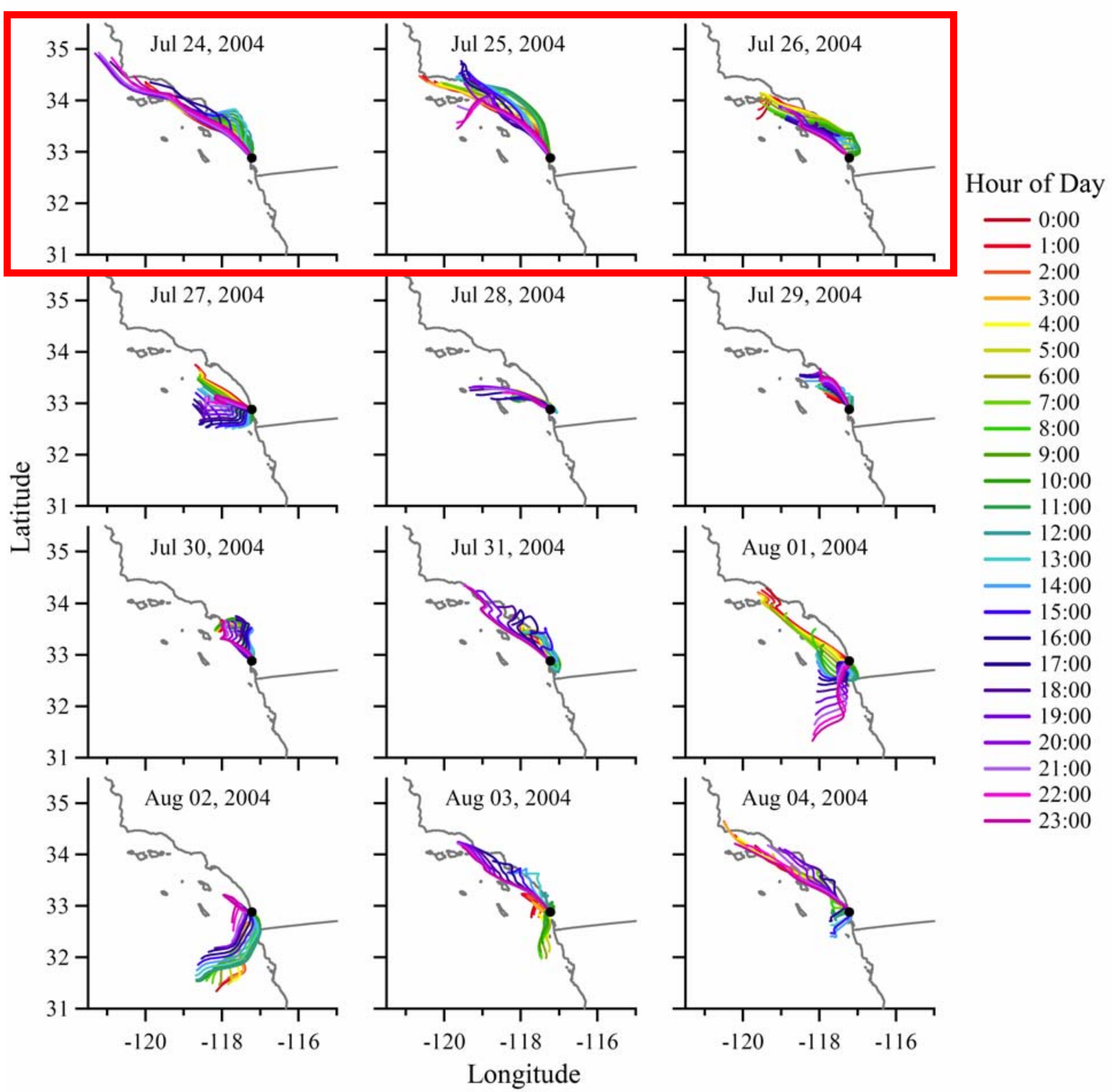
Toner, S.M., L.G. Shields, and K.A. Prather, Source apportionment of freeway-side $PM_{2.5}$ using ATOFMS, *Atmospheric Environment*, submitted, 2007.

San Diego Freeway Study (2004)
Impacts on PM



Total number fraction contribution to submicron mode = 10-58%

Regional Background Particle Types



Largest spikes occur when back trajectories came over LA / Long Beach (harbor regions)

SHIPS!

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Toner, S.M., L.G. Shields, and K.A. Prather, Source apportionment of freeway-side PM2.5 using ATOFMS, *Atmospheric Environment*, submitted, 2007.

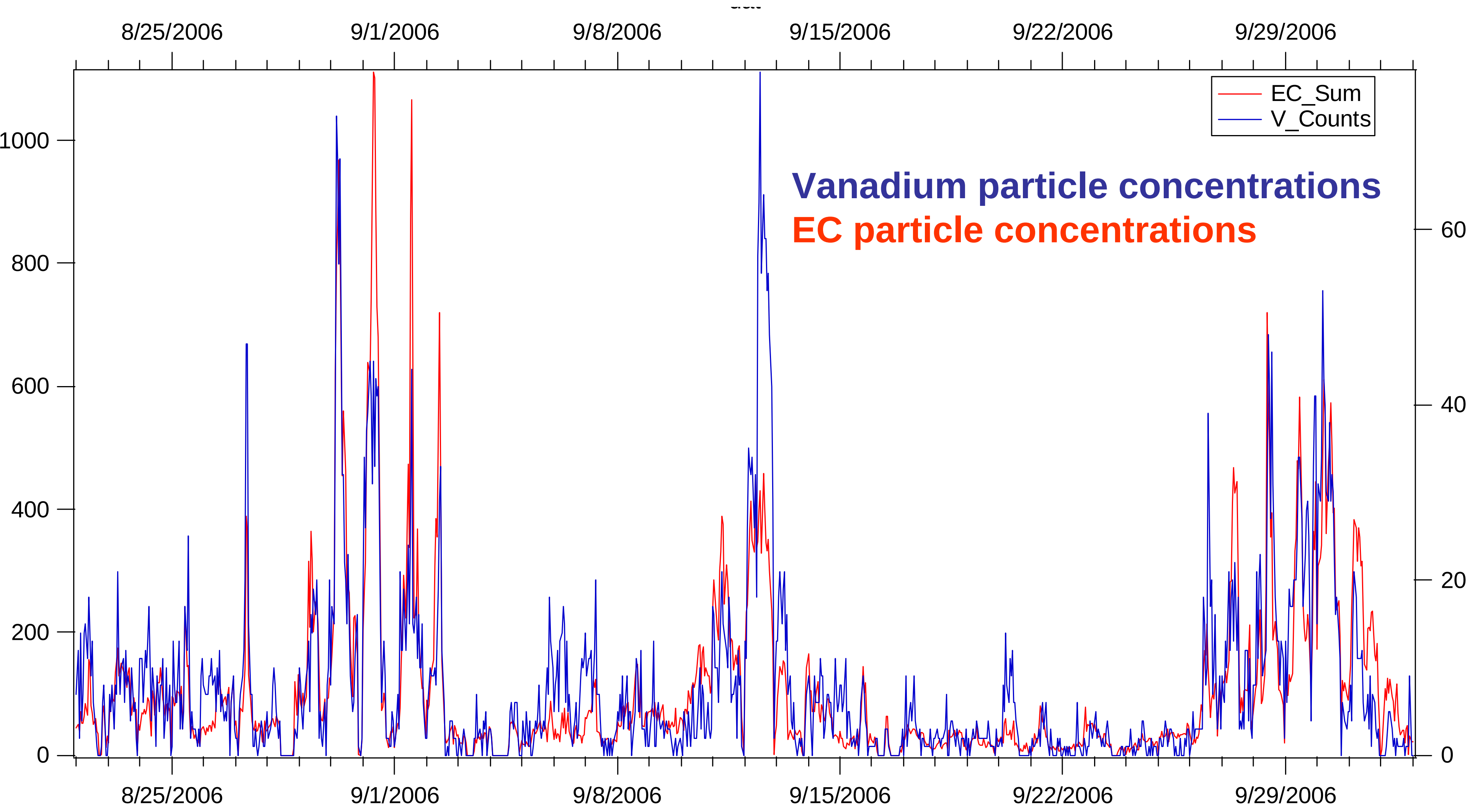
Freeway Results Summary

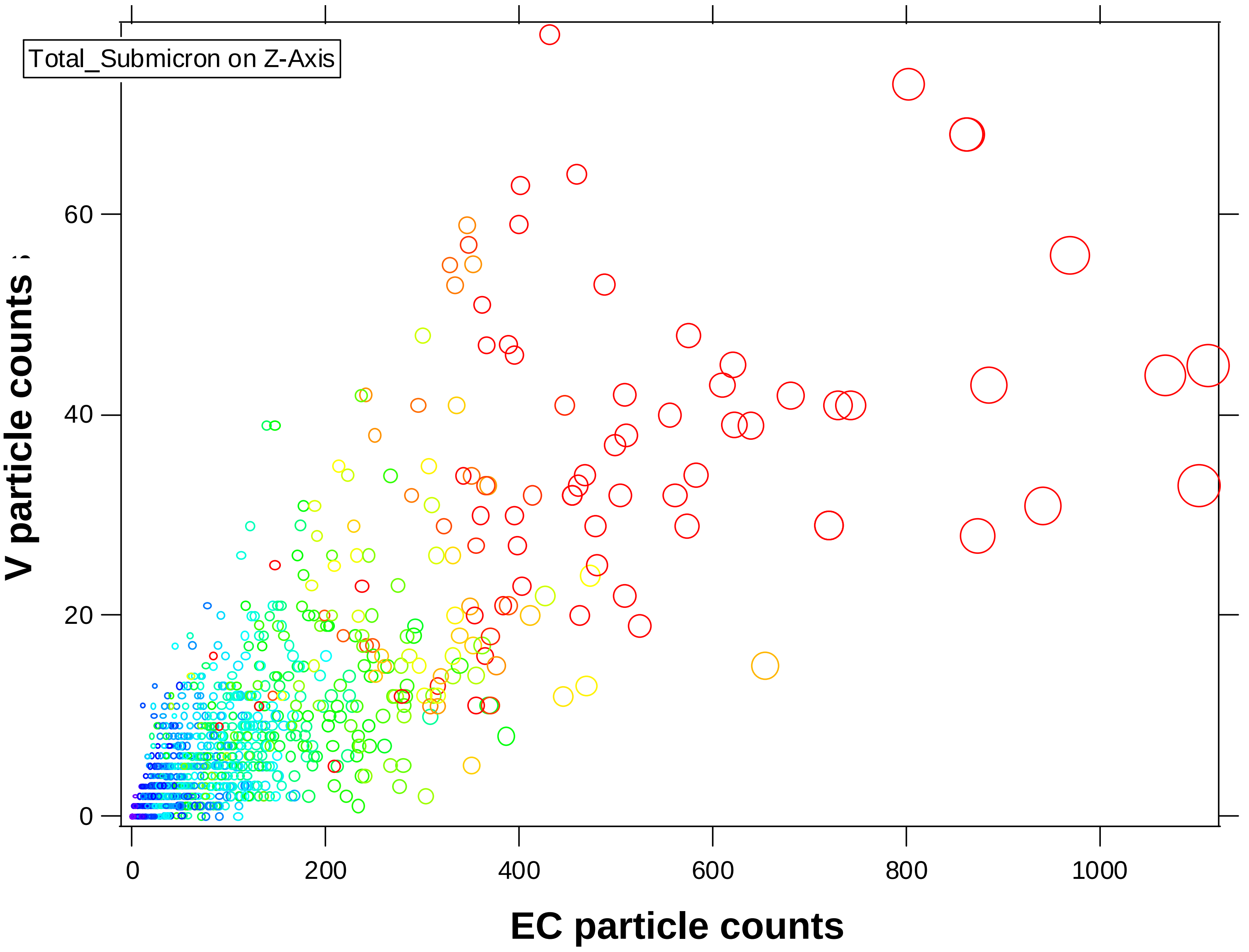
- The top particle types detected in the dynamometer studies match the top types detected next to the freeway
- HDDV dominate the vehicle emissions in UF mode despite lower traffic counts (consistent with previous studies)
- Weekday vs. weekend differences are observed
- Vehicle exhaust is <u>not</u> the only contribution to freeway-side aerosols
- Non-vehicle types become dominant with increasing size
- The source signature matching technique is capable of distinguishing between different sources, including HDDV and LDV


Riverside
Anaheim
Long Beach
Garden Grove
Santa Ana
Huntington Beach
Oceanside
SIO Pier
San Diego
Chula Vista
Tijuana
N
Image NASA
© 2007 Europa Technologies
Image © 2008 DigitalGlobe
©2007 Google™
44 mi
Pointer 33°11'41.50" N 117°37'32.58" W
Streaming |||||||||| 100%
Eye alt 150.99 m

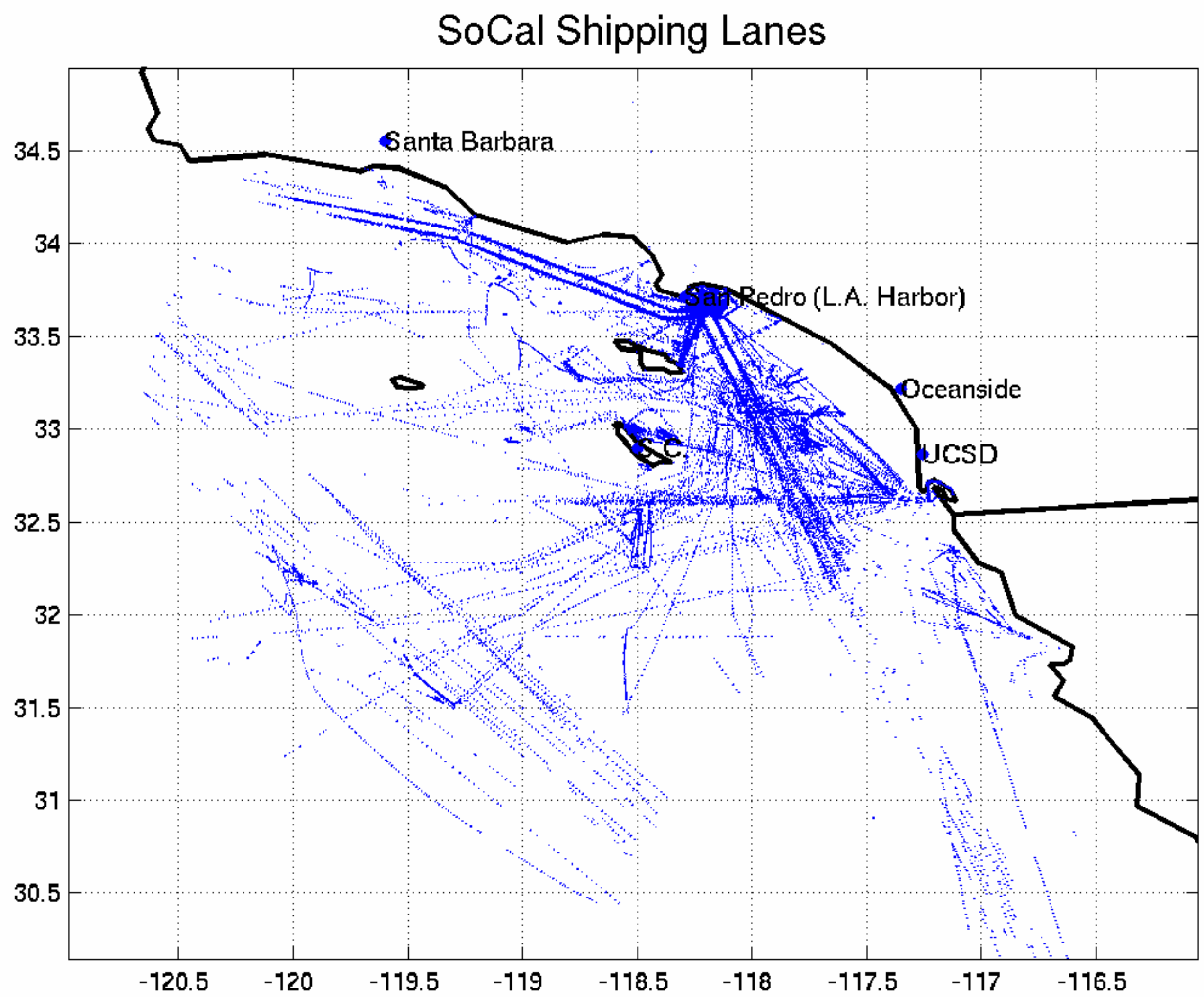

UCSD
I5 freeway
SIO pier
N
3213 ft
© 2007 Europa Technologies
© 2007 Google
Pointer 32°52'16.28" N 117°14'29.23" W
Streaming 100%
Eye alt 11119

2006 SIO pier study of ship impacts
8/24/2006-10/4/2006



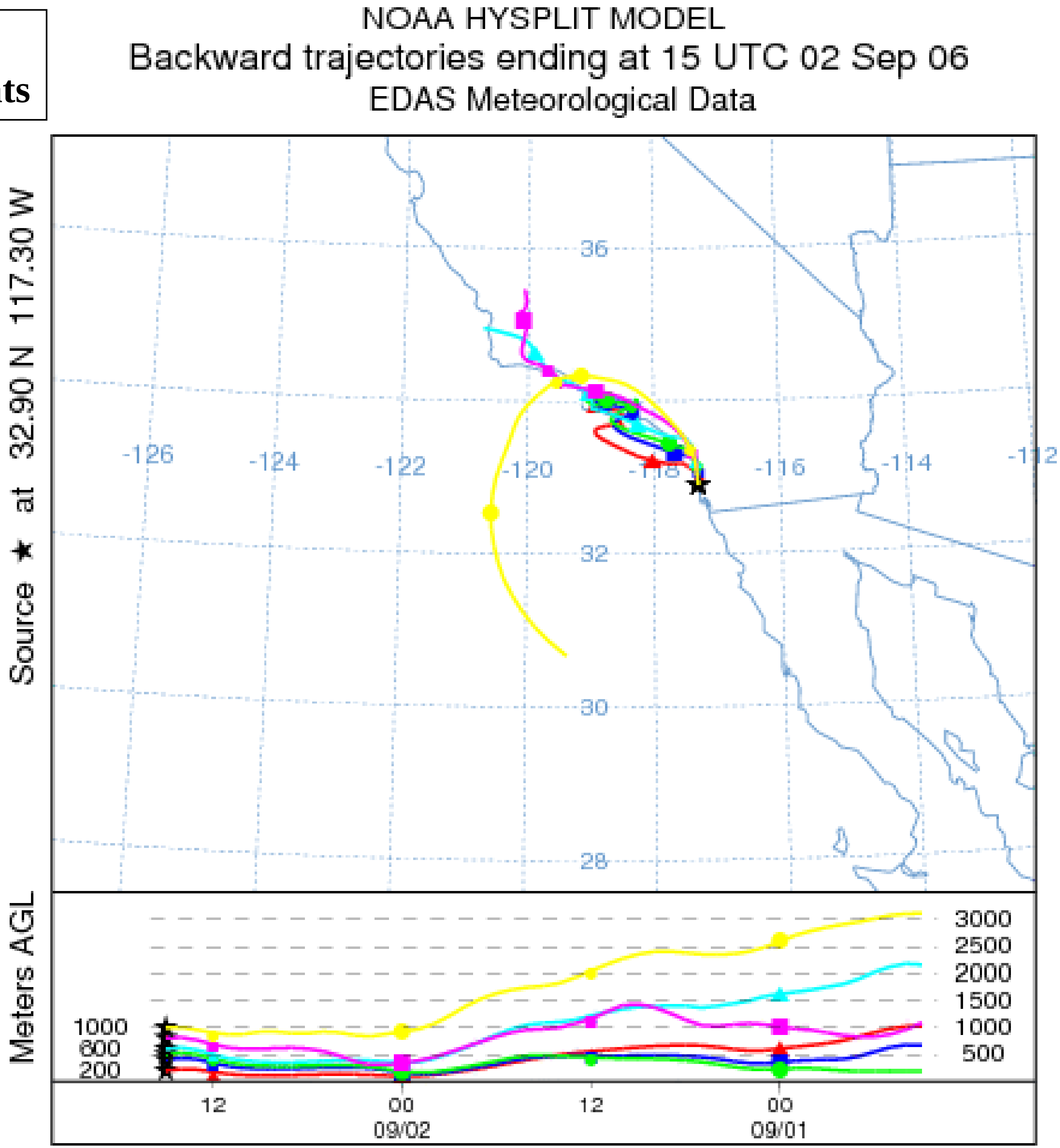


Z-axis (color and size) represents total submicron concentrations

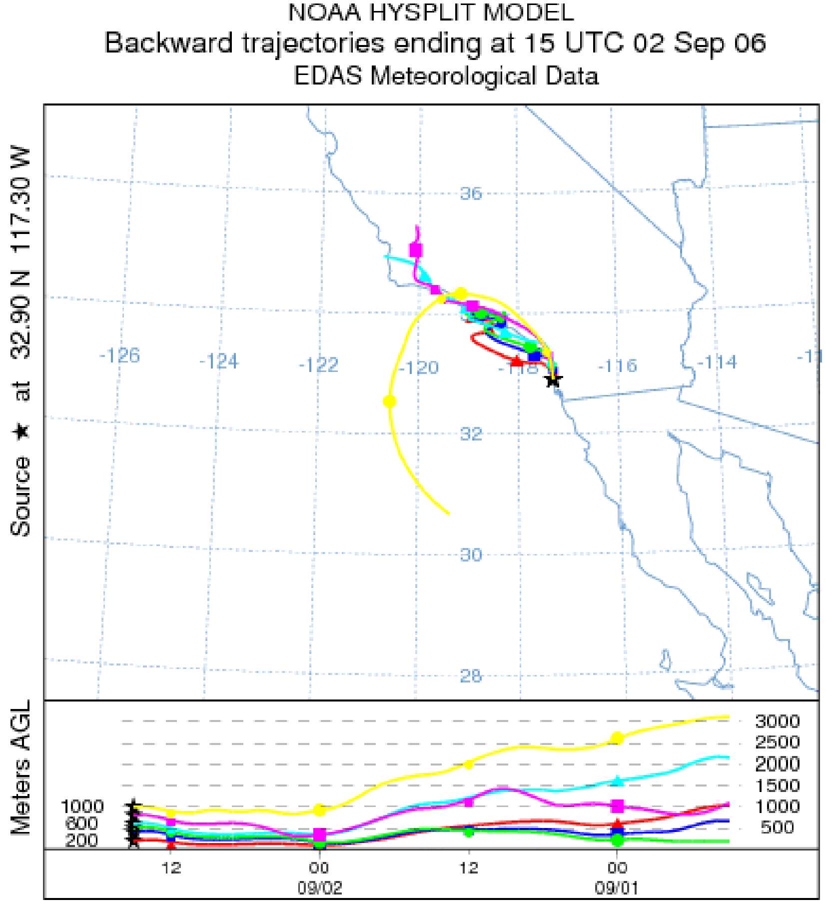


Ship data provided by Dr. Mark Thiemens group

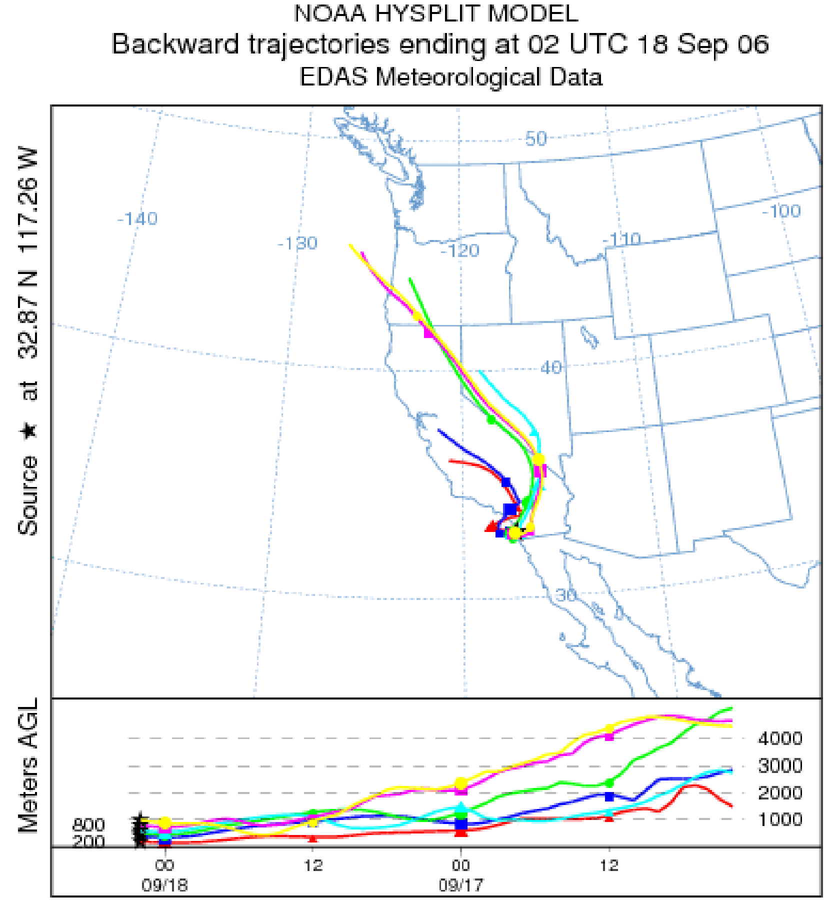
HYSPLIT
High V counts



During V period



During non V-period



HYSPLIT Comparison

- Can we apportion aged ambient particles?


Los Angeles
SOAR study
Lavic Lake
Summer
Summer
Fall
Fall

3rd Dimension: Aerosol Volatility

- **Thermodenuder experiment**

(in collaboration with Prof. Jose Jimenez & Alex Huffman)

– First thermodenuder-ATOFMS measurements

Core/shell model of an aged particle

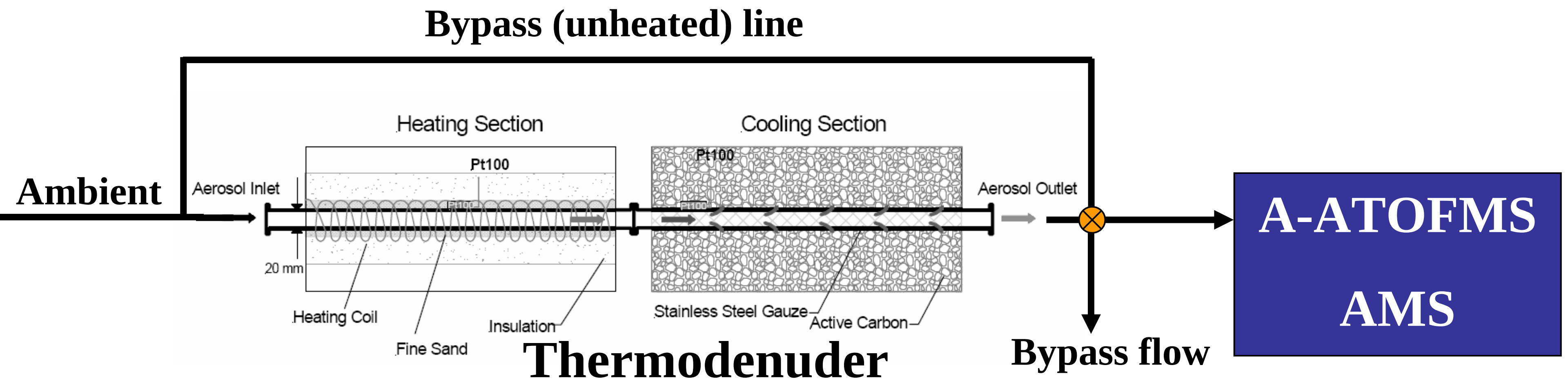
Chemical core = understanding of source

Difference = understanding of species' volatility/partitioning

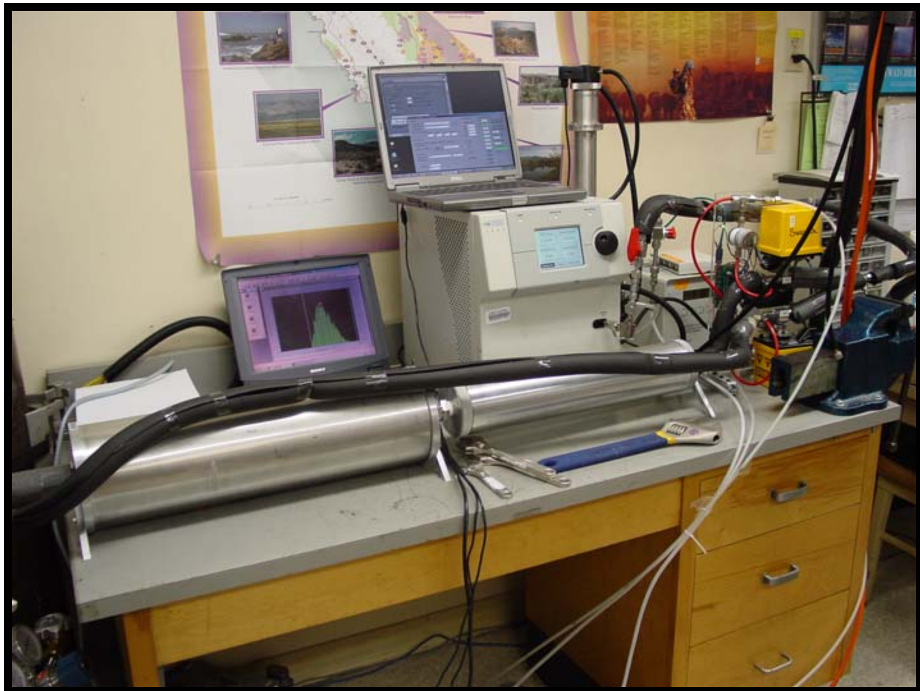
Temperature profile = greater understanding of chemical associations

– What is the chemistry of the cores of the particles?

Thermodenuder

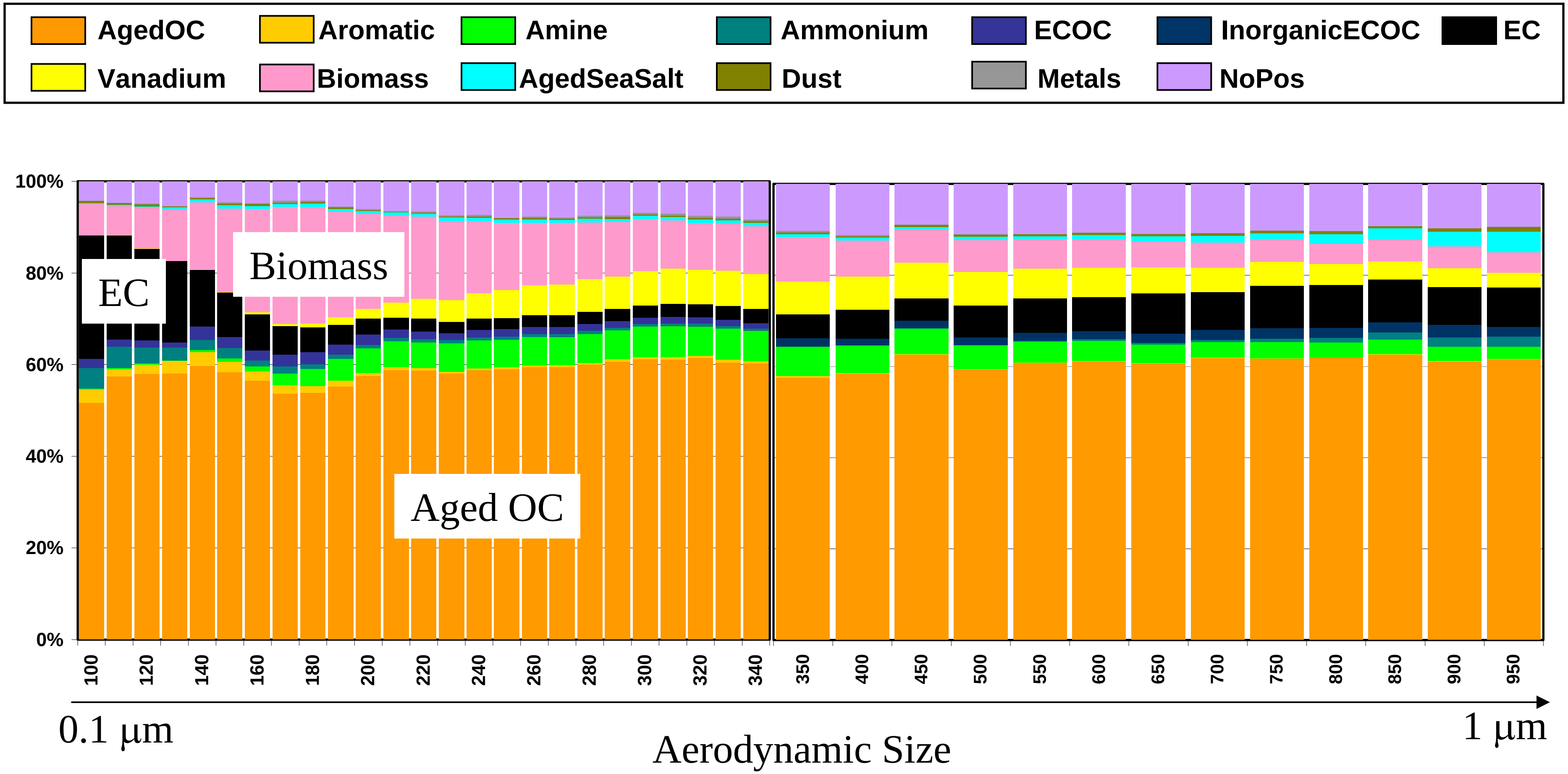


1. Switched between unheated ambient air and TD every 10 minutes
2. Sampled particles at set temperature (50°C, 75°C, 100°C, 125°C, 150°C, 175°C, 200°C) through TD

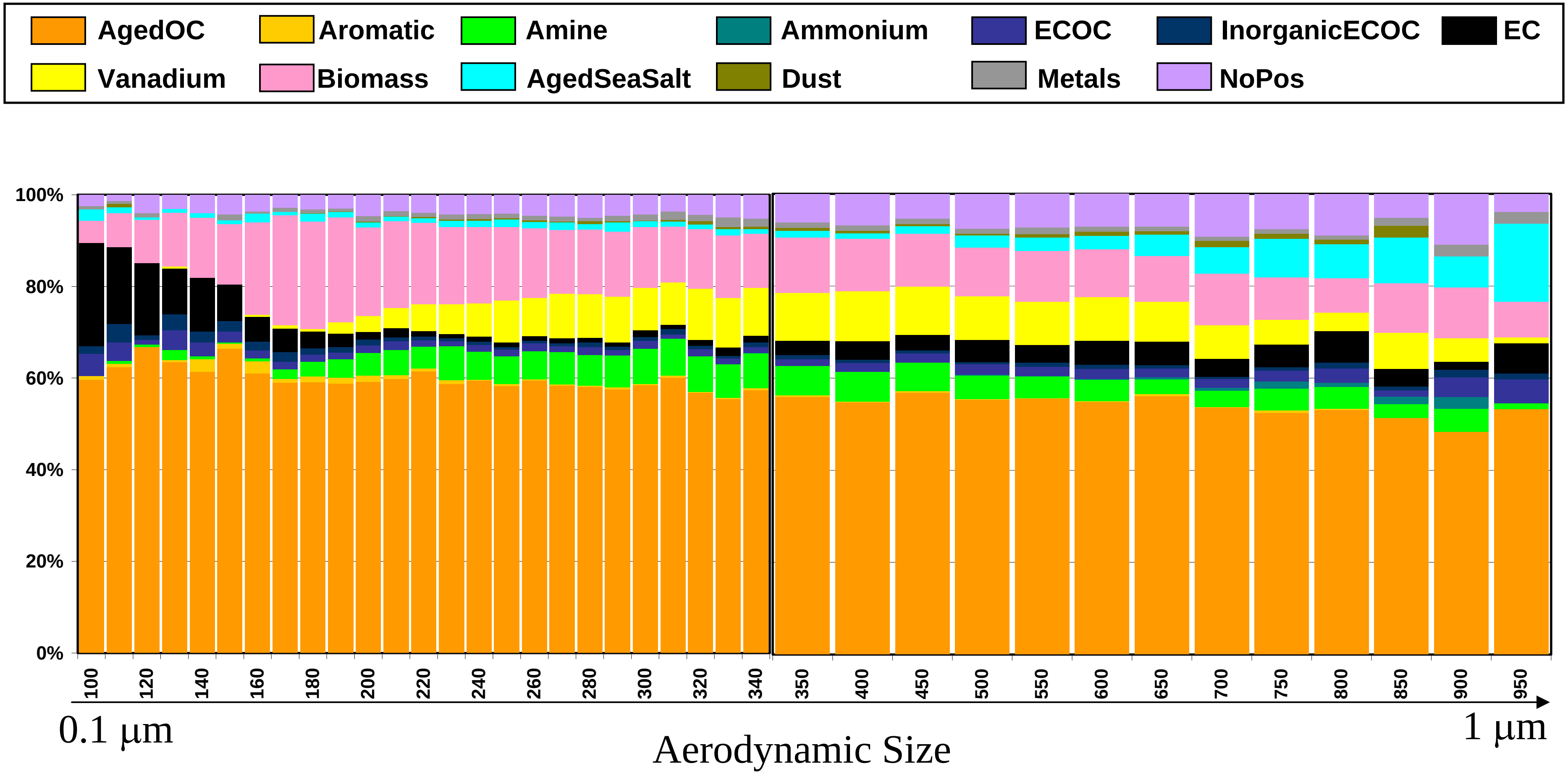


Wehner, B. et al., *Aerosol Science*. 2002.
Huffman, J.A. et al. *In Preparation*.

SOARII - Unheated

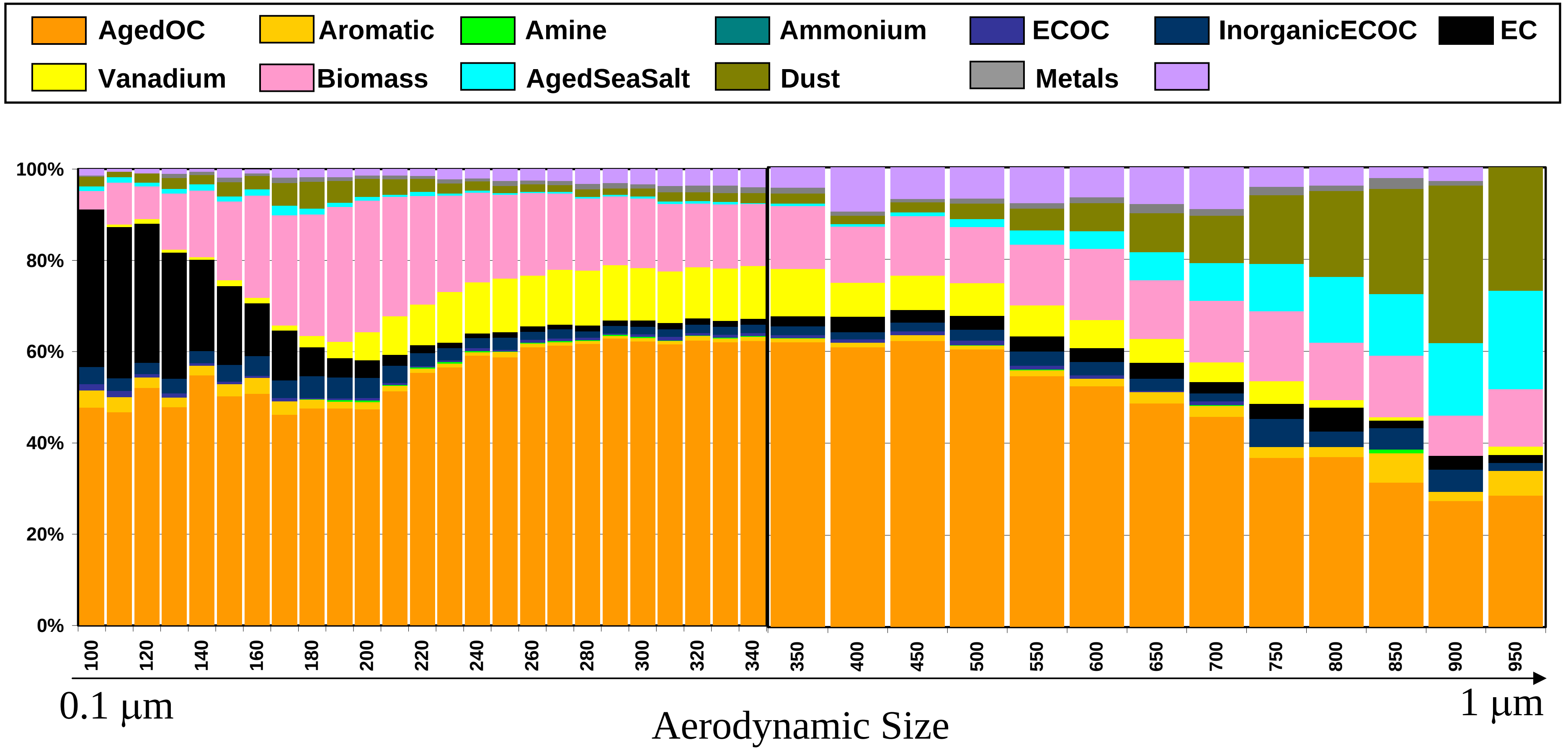


SOARII - 50°C



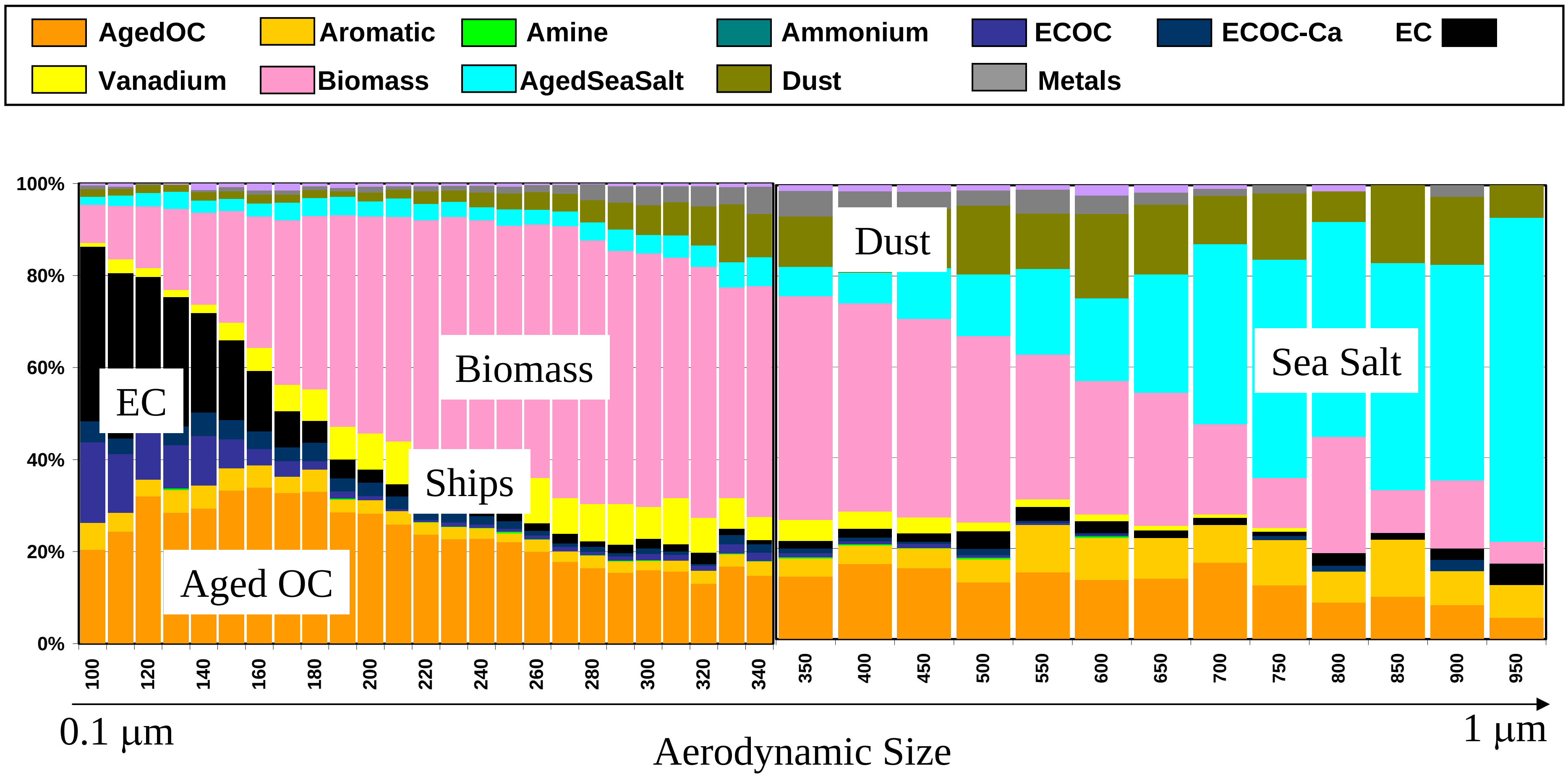
AgedOC
Aromatic
Amine
Ammonium
ECOC
InorganicECOC
EC
Vanadium
Biomass
AgedSeaSalt
Dust
Metals
NoPos
100%
80%
60%
40%
20%
0%
100
120
140
160
180
200
220
240
260
280
300
320
340
350
400
450
500
550
600
650
700
750
800
850
900
950
0.1 μm
1 μm
Aerodynamic Size

SOARII - 150°C



AgedOC
Aromatic
Amine
Ammonium
ECOC
InorganicECOC
EC
Vanadium
Biomass
AgedSeaSalt
Dust
Metals
100%
80%
60%
40%
20%
0%
100
120
140
160
180
200
220
240
260
280
300
320
340
350
400
450
500
550
600
650
700
750
800
850
900
950
0.1 μm
1 μm
Aerodynamic Size

SOARII - 200°C



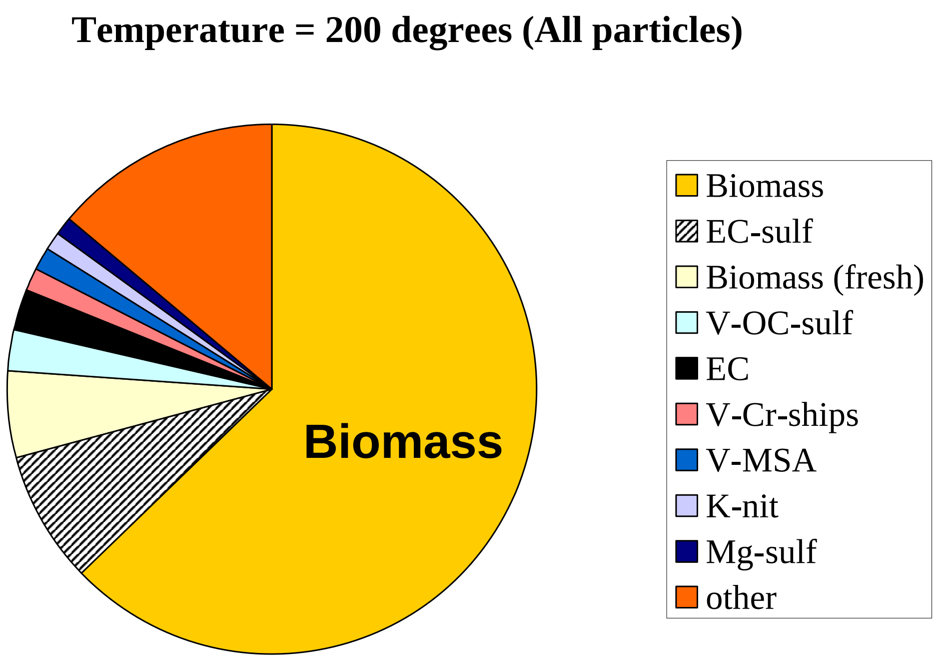
Observed seasonal impacts on volatility….

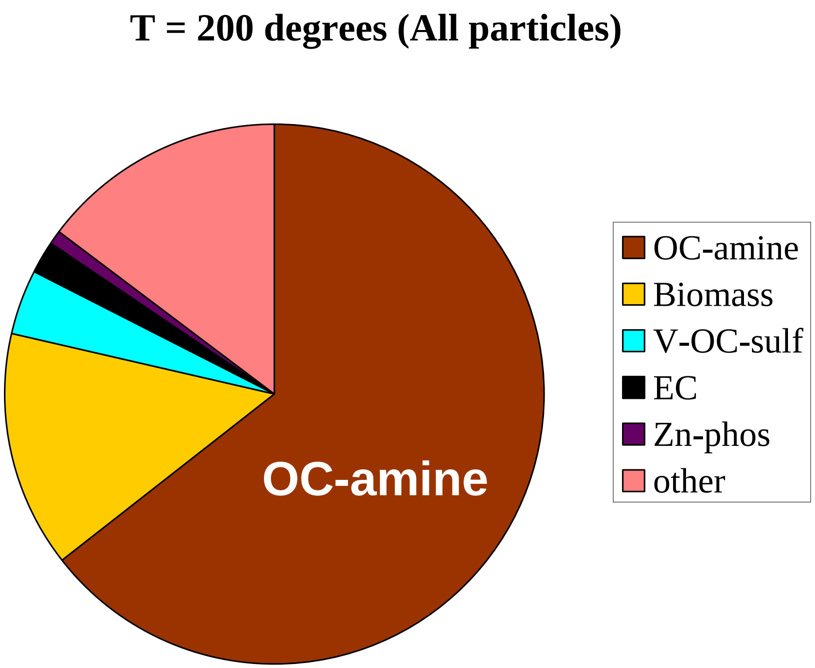
Do species come off of different types (cores) at different temperatures?

Core of biomass is relatively large (estimated 20-30% refractory material)

Fall

Summer

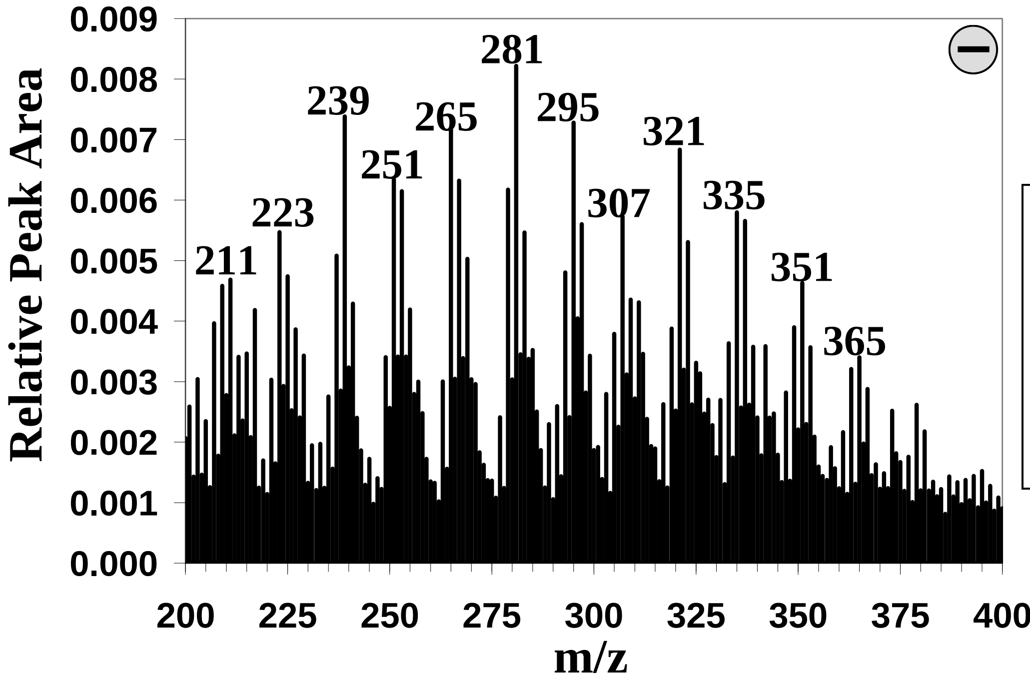




Less particles remain in detectable size range

- Amines are fully removed in the Fall
- Particles are more volatile in the Fall
- More “sticky” in the summer

Single Particle Core Chemistry (200 C)--Summer



Mass difference pattern of m/z 12, 14, and 16 (negative ions)

Real-Time, Single-Particle Measurements of Oligomers in Aged Ambient Aerosol Particles

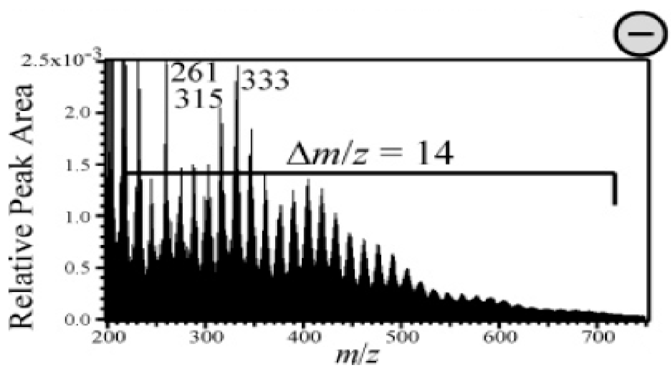
Denkenberger et al. ES&T (2007)

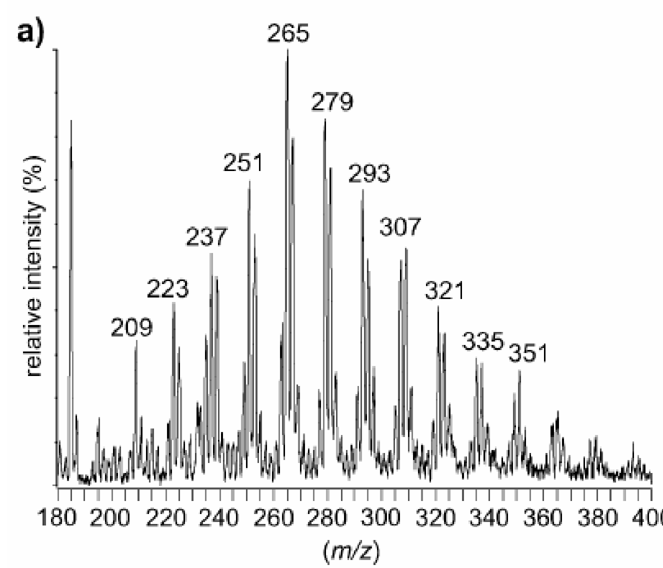
SOAR Filter Results:

Water-soluble sulfated (containing z -97, HSO_4^-) molecules

Chamber Comparison:

1,3,5-trimethylbenzene and NO_x, 52% RH

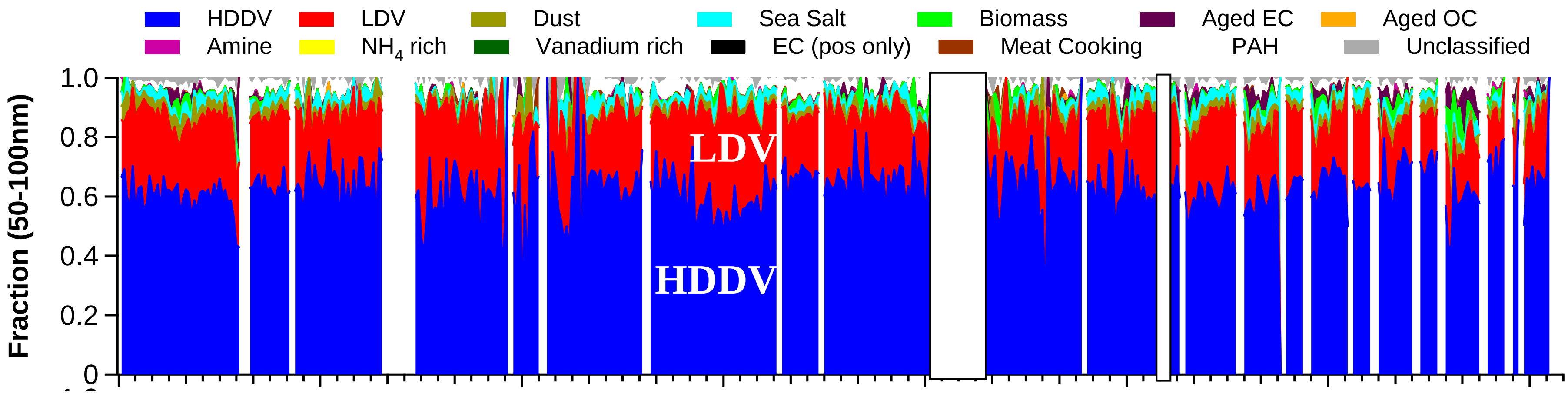




Gross et al., 2006, *Anal. Chem.;* Reemstma *et al.*, 2006, *Anal. Chem.*

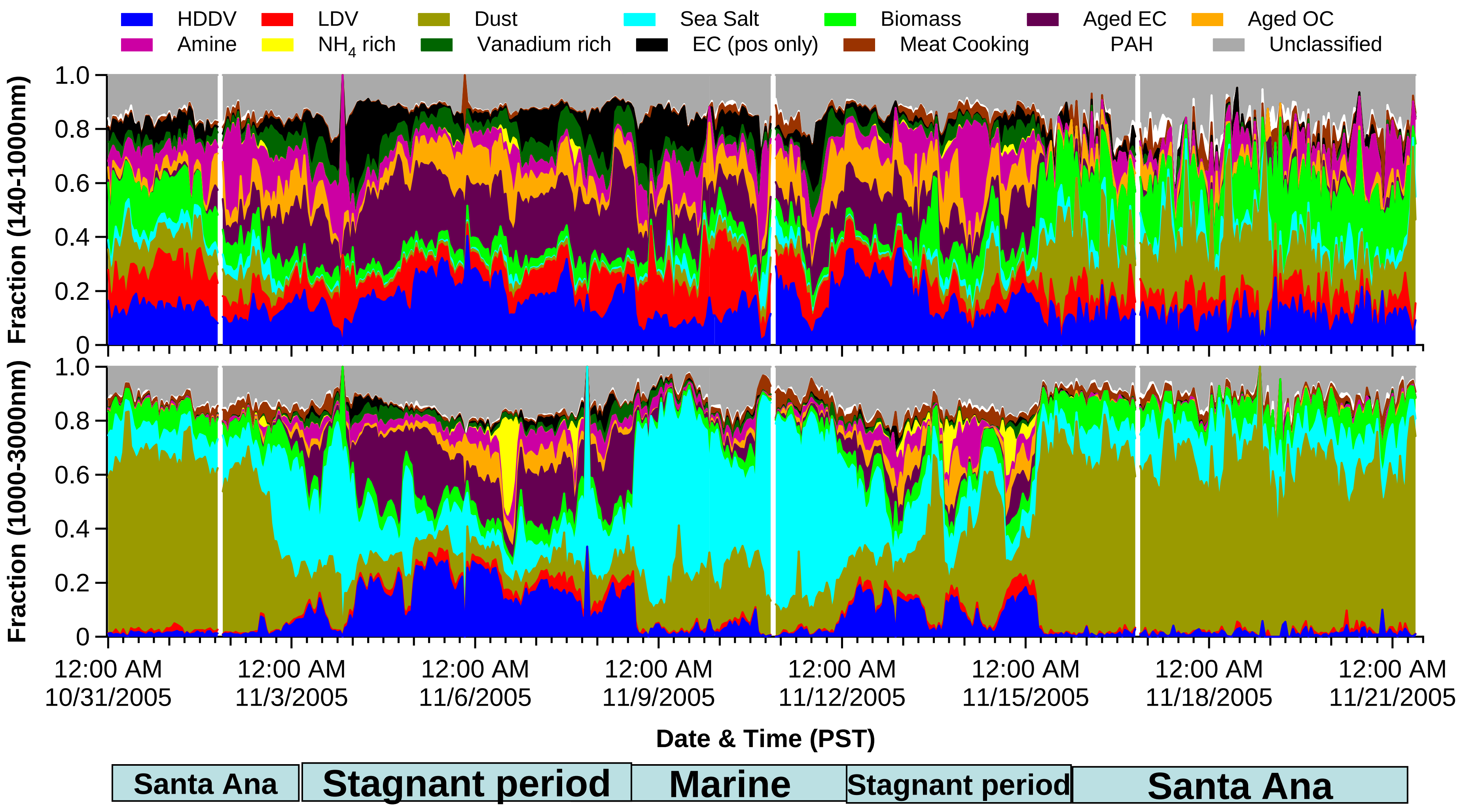
Ultrafine Particle Source Apportionment

Riverside--SOAR II – Fall (2005)



Source Apportionment

Fall-2005

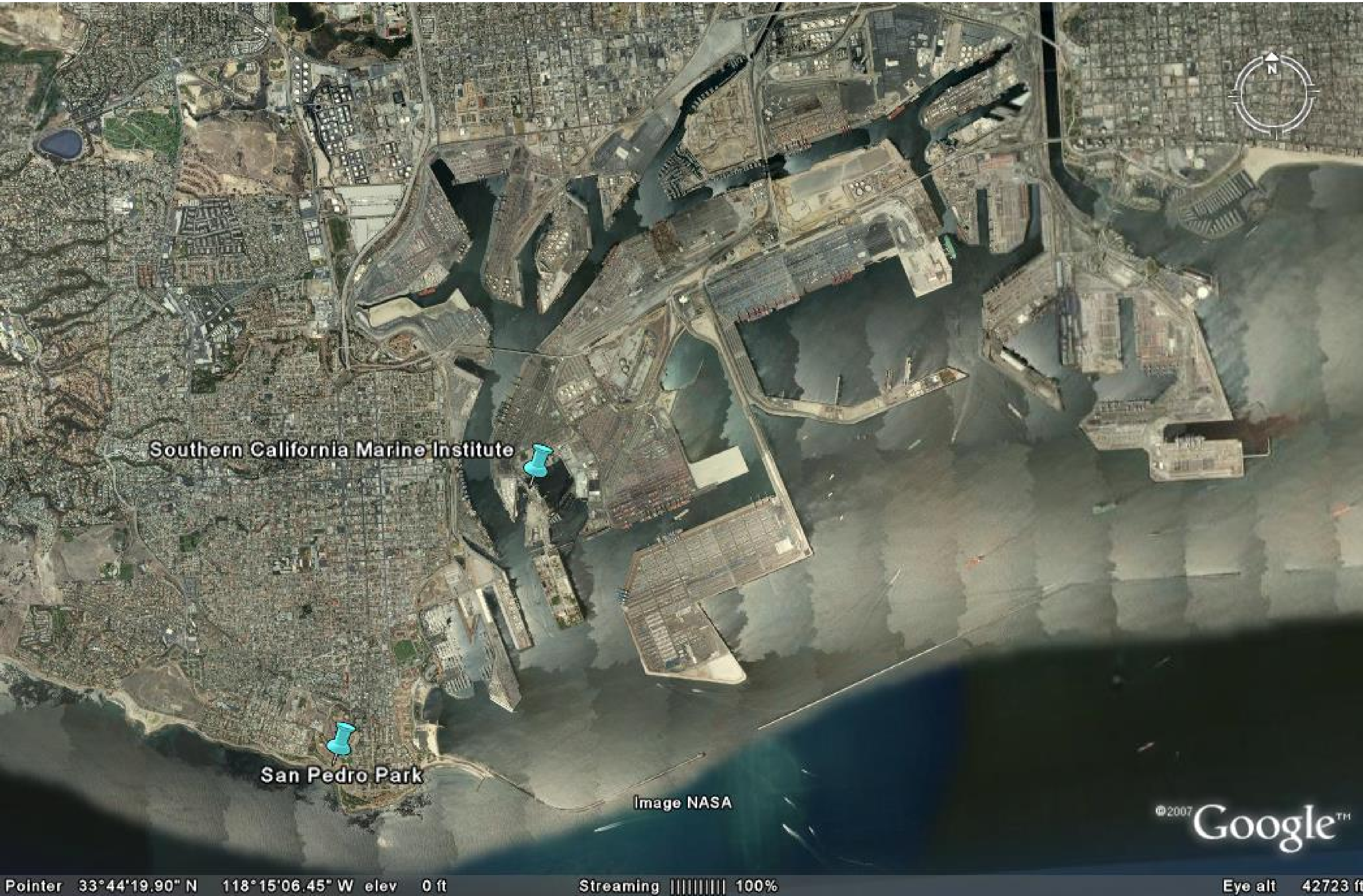


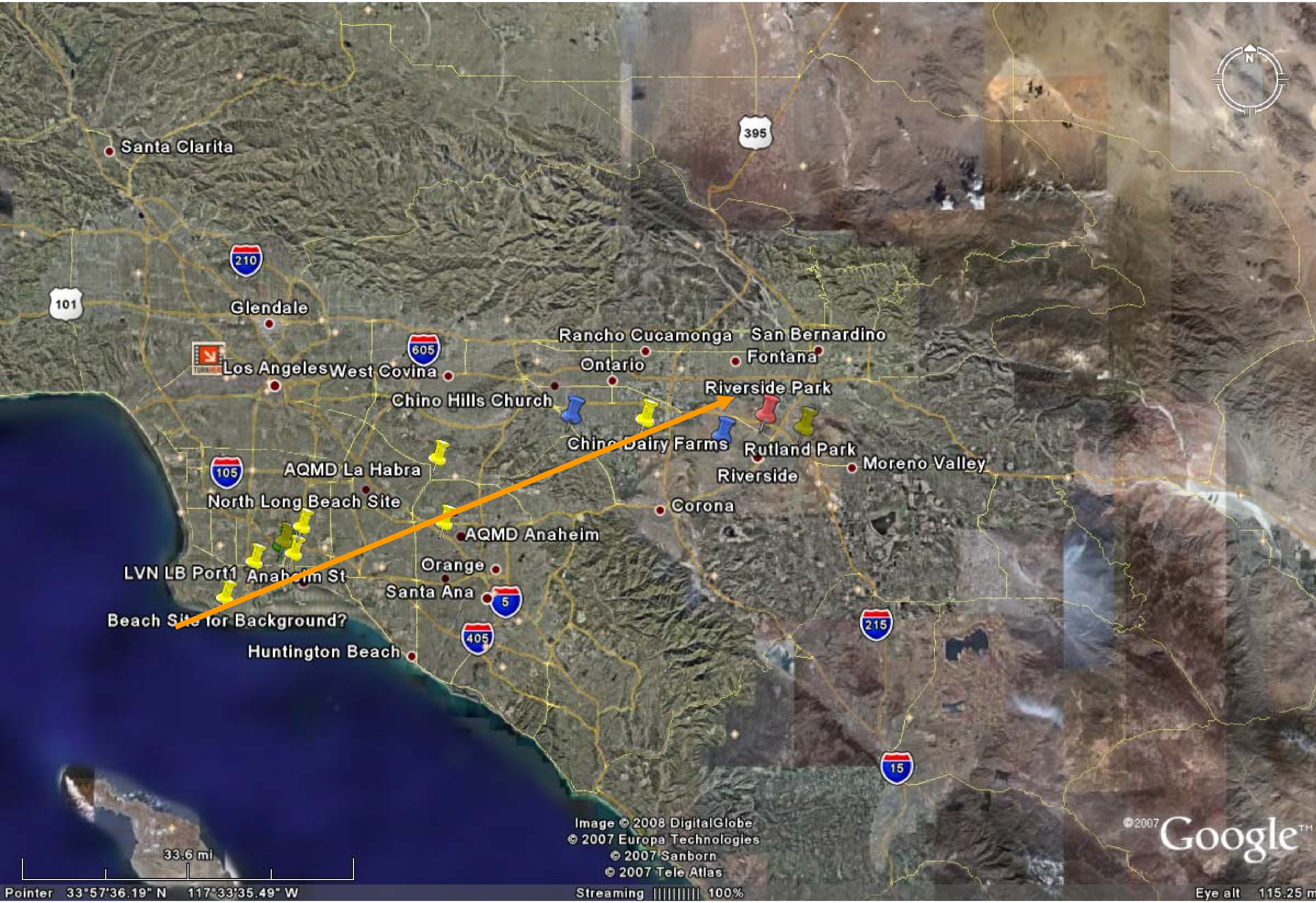
Conclusions

- Freeway study demonstrates potential for source apportionment of ambient particles with ATOFMS single particle library.
- Single particle mass spectrometry can be used to ID mass/number fractions from various sources (dust, biomass, salt, industrial emissions, cars, trucks)
  - Segregate by time, size, mixing state (source, aging)
  - Size resolved source fractions
  - Ultimately, determine distributions of the masses of secondary species among different particle types
- "On the fly" source apportionment now being used in field
  - Allows selective sampling of aerosol
  - Link with health effects studies
- Thermodenuder-ATOFMS effective way to remove aged shell so core of particle can be apportioned
  - Examine ratio of mass of core/source to secondary species (1^{o} vs. 2^{o})
- Mobile laboratory being used to study spatial and seasonal distribution of particulate matter in California


pace
SVA

LA/LB Ports


Southern California Marine Institute
San Pedro Park
Image NASA
©2007 Google™
Pointer 33°44'19.90" N 118°15'06.45" W elev 0 ft
Streaming ||||||||| 100%
Eye alt 42723 ft



Santa Clarita
210
101
Glendale
395
Rancho Cucamonga
San Bernardino
605
Fontana
Los Angeles
West Covina
Ontario
Riverside Park
Chino Hills Church
Chino Dairy Farms
Rutland Park
Moreno Valley
105
AQMD La Habra
Riverside
North Long Beach Site
Corona
AQMD Anaheim
Orange
LVN LB Port1
Anaheim St
Santa Ana
5
Beach Site for Background?
215
405
Huntington Beach
15
Image © 2008 DigitalGlobe
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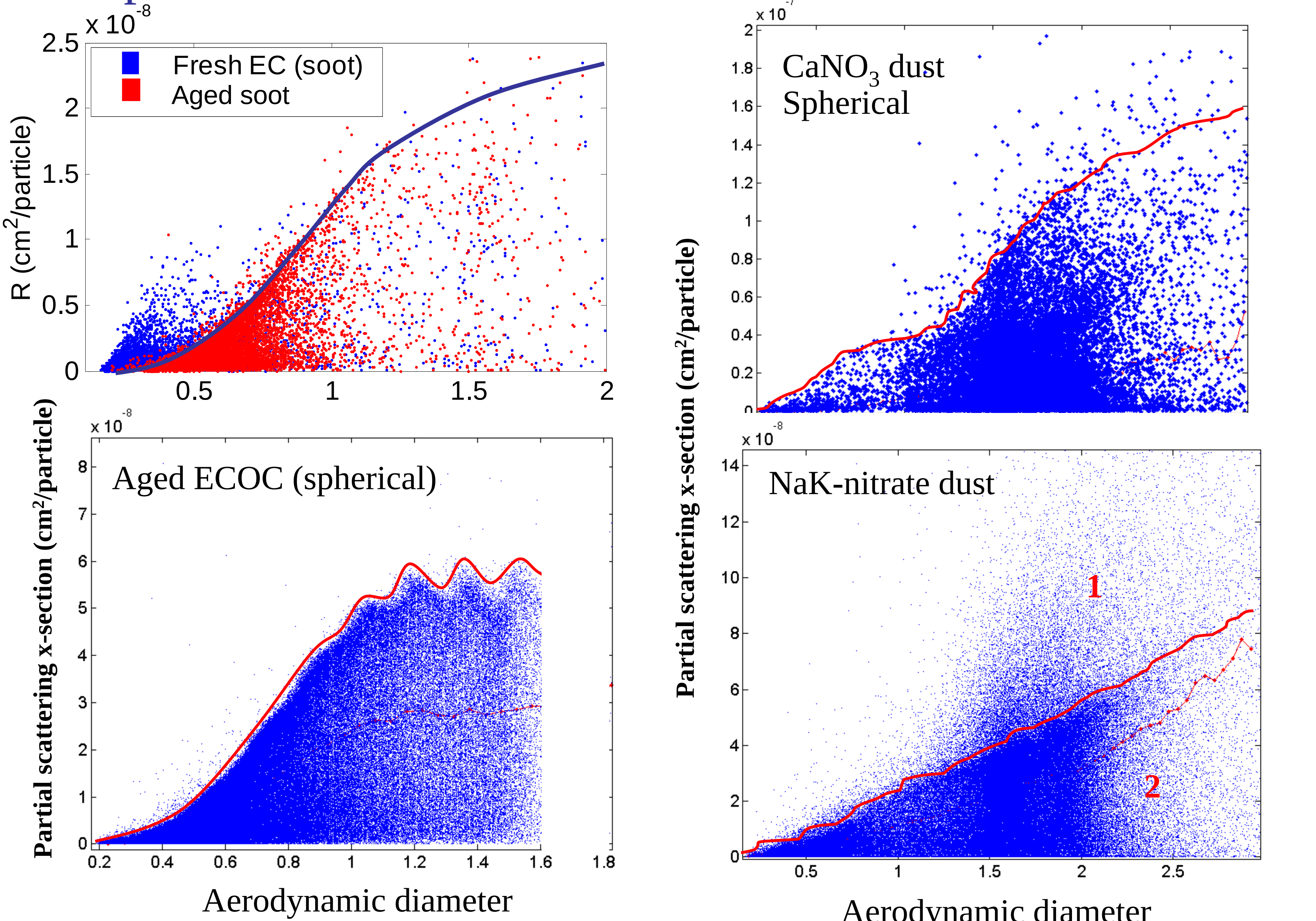
©2007 Google™
33.6 mi
Pointer 33°57'36.19" N 117°33'35.49" W
Streaming 100%
Eye alt 115.25 m

Ongoing studies

- Using source library in studies around the world (Mexico, Korea, China, Europe, Athens)

- Source impacts on climate
  – Cloud formation (aircraft studies)
  – Optical properties

Optical measurements linked with size and mixing state



Moffet et al. submitted to JGR, 2007

Ongoing studies

- Using source library in studies around the world (Mexico, Korea, China, Europe)

- Source impacts on climate
  - Cloud formation (aircraft studies)
  - Optical properties

- Health effects of specific sources (U. of Rochester)
  - segregate aerosols by time, size, and source
  - fresh vs. aged

Acknowledgements

- California Air Resources Board
- The entire Prather group

<u>Source and ambient studies</u>

- Andy Ault
- Laura Shields
- Joseph Mayer
- Ying Yang
- Melanie Zauscher
- Maggie Yandell
- Cassie Gaston
- Kerri Pratt
- Dr. Bob Moision
- Ryan Sullivan
- Meagan Moore

- Dr. Steve Toner, Dr. Sharon Qin, Dr. Matt Spencer, Dr. Ryan Moffet
- Dr. David Sodeman, Dr. David Suess